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ON THE ACQUISITION OF ATMOSPHERIC NITROGEN BY PLANTS.

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The problem of the ways in which nitrogen becomes a part of living organisms, though a fundamental one in biological chemistry, cannot yet be regarded as solved. It reduces itself, however, to the question of the sources of the nitrogen of plants.

The prevalent, though not universal, opinion among chemists and vegetable physiologists appears to be that the free nitrogen of the air is not assimilated by plants, and that the proportions of combined nitrogen (ammonia, and nitric and nitrous acids) in the atmosphere are so minute that the amounts which ordinary plants could absorb during their growth must be unimportant. It is hence inferred that plants obtain no considerable part of their nitrogen directly from the air, through their leaves, and that nearly or quite all must come to them in nitrogen compounds from the soil through their roots.

There are, however, a number of considerations in the way of an unreserved acceptance of this view. It is very difficult to explain how certain plants, the legumes especially, obtain their nitrogen, if not from the air. That plants may not assimilate considerable quantities of nitrogen compounds from the atmosphere is not absolutely proven. In the classic experiments of Boussingault and of Lawes, Gilbert and Pugh, which are commonly

regarded as most decisive against the assimilation of the uncombined nitrogen of the air, the plants had, in the majority of the instances, very inadequate supplies of food, and the arrangements were such as may perhaps have excluded the action of electricity, which, as recent experiments by Berthelot imply, may effect the assimilation of free nitrogen.

The following experiments indicate that some plants, at any rate, may, when grown under normal conditions, obtain in some way and assimilate large quantities of atmospheric nitrogen.

The principal question proposed for study was this:

May plants, grown under normal conditions, acquire any considerable amount of nitrogen, free or combined, from the ambient atmosphere?

After a series of trials had shown a not inconsiderable acquisition of atmospheric nitrogen, a second series was planned to verify the results of the first and to include a collateral inquiry:

How is the acquisition of nitrogen from the atmosphere affected by abnormal conditions of growth, and what bearing may the results obtained have upon the interpretation of those obtained by other experimenters, and upon the general question of the assimilation of atmospheric nitrogen by plants?

Plan of the Experiments.

The experiments were made by growing peas in sand which had been purified by washing and igniting,[1] and to which were applied nutritive solutions containing known quantities of nitrogen. The amounts of nitrogen supplied in nutritive solutions and seed were compared with the amounts found at the end of the experiment in residual solution and plants. The excess of the latter amount over the former, in some cases very large, must represent nitrogen acquired, in some way, from the atmosphere.

The conditions of growth were varied in the second series:

1st. By varying the concentration of the nutritive solutions from one part by weight of dissolved salts to five or six in one thousand of solutions. (One part per thousand has, in other experiments, been found most favorable to normal growth, while two parts or more per thousand have been observed to retard or prevent assimilation and growth.[2])

[1] See Appendix. [2] See remarks concerning Table II, beyond.

2d. By varying the total quantity of food supplied to the roots by the solutions, from an amount seemingly sufficient, or nearly so, for normal growth, to a very scanty supply.

3d. By varying the proportion of nitrogen in the solution, making it in some cases rather small, in others very small as compared with the amount of mineral food. In this way the plants were enabled to make some growth at the expense of the nitrogen furnished to the roots, and left to gather the rest of their nitrogen, if they should so choose, from the air.

For pots in which to cultivate the plants, ordinary glass bottles of from one to three litres capacity were employed. The bottom of each was cut off and the bottle turned neck downwards. A watch glass was then inverted over the neck and the sand poured in. The pots were enclosed in wooden boxes so constructed as to exclude the light, and at the same time to permit a glass beaker to be placed under the bottle to catch any solution or sand which might accidentally run through. This simple and inexpensive arrangement served its purpose most satisfactorily, an especial advantage seeming to me to be the ease with which the water supply is regulated so as to keep the sand nearly saturated without preventing the circulation of air through it.

The nutritive solutions were such as are ordinarily used in water and sand culture. They contained potassium and calcium nitrates, potassium phosphate, magnesium sulphate and ferric chloride. The water used for the nutritive solutions, for watering the plants, and for separating the plants and residual solutions from the sand at the end of the experiments, was carefully freed from nitrogen compounds.[1] The plants were grown in the open air, but protected from rain and dew by being put under cover at night and in rainy weather. The nitrogen in seeds and in plants was determined by the soda-lime method, that in the nutritive solution by the method of Schulze-Tiemann. The only considerable source of error in the experiments seemed to be in a probable loss of nitrogen, perhaps by decomposition of the nitrates in presence of germinating seeds, as observed by Boussingault,[2] though possibly from decomposition of the seeds during germination and growth, especially in the trials in which the solutions were concentrated. This would tend to reduce the amount of nitrogen found at the end of the

[1] See Appendix.

[2] Ann. chim. Phys. [5] **22**, 1881, 433.

experiment, and thus make the apparent gain of nitrogen less than the amount actually acquired by the plants from the atmosphere.

Two series of experiments were made, both with peas of the "dwarf" variety called "Early Philadelphia." The first was tentative, but showed in every case an excess of nitrogen at the end of the experiment over that contained in solution and seed. The experiments of the second series were more detailed, and gave larger gains of atmospheric nitrogen.

Experiments with Peas. First Series.

The plants of this series were grown in a greenhouse. The solution used was essentially the same as employed by Fittbogen in sand culture.[1] Instead, however, of the usual concentration 1 : 1000, it was found more convenient to prepare solutions of the concentration of 1 : 100, and dilute them as used. For this purpose the salts were dissolved in two or more separate portions to avoid precipitation. Thus in the First Series, "Solution I" contained potassium phosphate and nitrate, and "Solution II" calcium nitrate and magnesium sulphate, while ferric chloride was applied separately. The seeds, previously sprouted, were put in the sand March 26th. Solutions I and II were applied at the same time, water being added to dilute the solutions, and water was applied at intervals during growth to replace that withdrawn by the plants and by evaporation from the solution. The water-holding capacity of the sand, previously tested, was such as to permit the dilution of the solution to considerably over one thousand parts of water to one of salts. At the outset nearly as much water was added as the sand would hold, but during growth there were probably times when the solutions were so concentrated by evaporation as to make the proportion of dissolved salts much more than 1 : 1000.

With these preliminary statements, the statistics of the experiments, given in Table I herewith, will be easily understood.

TABLE I.—Experiments with Peas. First Series.

Statistics of Seed, Solutions, Planting, Produce, etc.

Number of Exp't.	Date of Planting.	Weight of Sand.	Number of Seeds.	Weight of Seeds.	Solution I Added.	Solution II Added.	Total Solution Added.
A	March 26	2.5 kilos.	6	1.4829 grams	40 cc.	40 cc.	80 cc.
B	"	2.5 "	4	1.0927 "	60 cc.	60 cc.	120 cc.
C	"	2.5 "	4	1.0675 "	40 cc.	40 cc.	80 cc.

[1] Versuchs-Stationen, **13**, 81.

Number of Exp't.	Date of Harvesting.	Number of Plants Matured.	Average Height of Plants.	Number of Peas.	Weight of Vines, Leaves, Fruit, etc.	Weight of Roots and Adhering Sand.	Total Weight of Plants.
A	May 27	6	60 cm.	18	6.9 grams.	4.9 grams.	11.8 grams.
B	June 7	4	77 "	16	5.8 "	5.2 "	11.0 "
C	May 27	4	70 "	12	4.3 "	14.5 "	18.8 "

Nitrogen Statistics.

Number of Exp't.	Nitrogen supplied at beginning of Experiment.			Nitrogen found at End of Experiment.			Gain of Nitrogen.
	In Seed.	In Nutritive Solution.	Total.	In Residual Solutions.	In Plants.	Total.	
A	49.5 mgr.	61.4 mgm.	110.9 mgm.	7.2 mgm.	167.2 mgm.	174.4 mgm.	63.5 mgm.
B	36.4 "	92.2 "	128.6 "	8.0 "	133.8 "	141.8 "	13.2 "
C	35.6 "	61.4 "	97.0 "	1.3 "	108 7 "	110.0 "	13.0 "

Besides the Nos. A, B and C, the series included two others, D and E, into which, unfortunately, a quantity of rain-water fell through a leak in the roof of the greenhouse during a violent shower. The water percolated through the sand and was caught in the beakers below. The accident was discovered by the gardener who had been charged to watch the plants, and who poured the contents of the beakers back upon the sand before either the assistant in charge of the experiments or myself had learned of the matter. One of the pots received more rain-water than the other, and more fell into the beaker below. The analysis at the end of the experiment showed in one case a loss of nitrogen and in the other a very large gain. The average of the two gives a gain of nitrogen not widely different from the average gain in the other three, A, B and C. It seems to me very probable that in pouring the percolated solution back into the pots the gardener may have changed the beakers, emptying that under pot D into pot E, and *vice versa*. If so, this would readily account for the discrepant results in D and E. The nitrogen statistics of these are as follows:

Number of Exp't.	Nitrogen supplied.			Nitrogen found.			Gain + or Loss — of Nitrogen.
	In Seed.	In Solution.	Total.	In Plant.	In Residual Solution.	Total.	
D	16.66 mgm.	92.17 mgm.	108 83 mgm.	94.19 mgm.	3.10 mgm.	97.29 mgm.	—10.15 mgm.
E	15.25 "	61.44 "	76.69 "	82.52 "	56.82 "	139.34 "	+62.65 "
D + E'	31.91 "	153.61 "	185.52 "	176 71 "	59.92 "	236.63 "	+52.50 "

It would, of course, be unwarrantable to include these experiments with those described above (A, B and C), and, for that matter, the possibility of such an accident casts a suspicion upon the whole series, so that their results can be entitled to full credence only on condition of their being verified by repetition under circumstances fitted to preclude such sources of error. Nevertheless, the facts that the trials in which there were no apparent sources of uncertainty showed large gains of nitrogen, amounting in A to 38 per cent. of the total nitrogen of the plants, and that the average of C and D tallies with that of A, B and C, hardly leave room for doubt that the plants did somehow obtain a considerable portion of their nitrogen from the air. The results thus obtained seemed, therefore, to warrant farther and more detailed experiments.

Experiments with Peas. Second Series.

Accordingly, the following spring, a small building was erected and provided with large doors and movable tables, upon which the plants could stand, and be moved out and in at will. The immediate care of the experiments was entrusted to an assistant, who lived close by, and whose duty included moving the plants into the open air in the morning and back under cover at night and whenever there was a prospect of rain. The plants were thus carefully and constantly watched and protected from rain and dew.

The general arrangement of the experiments was similar to that of the first series. The nutritive solutions were prepared by dissolving each salt separately. The separate solutions were as follows, each containing (approximately) 1 gram of the water-free salt in 100 cc.:

Solution "NI," $Ca(NO_3)_2$.
Solution "NII," KNO_3.
Solution "NIII," $Ca(NO_3)_2 + KNO_3$ (NI and NII mixed).
Solution "P_2O_5," K_2HPO_4.
Solution "Mg," $MgSO_4$.
Solution "Fe," Fe_2Cl_6.

All the pots received like quantities of Solutions "P_2O_5," "Mg" and "Fe." One half, Group I, six pots, received nitrogen in Solution "NI." The other half, Group II, six pots, received

nitrogen in Solutions "NI" and "NIII." The mixture given to Group I was called the "Smaller Nitrogen Ration"; that of Group II, the "Larger Nitrogen Ration." One-third of the pots had 1 kilogram of sand, one-third 2 kilos, and one-third 3 kilos, each. One half of the pots of each group had three plants, the others six plants each. The arrangements and results of the experiments appear in the tables of statistics herewith.

TABLE II.—EXPERIMENTS WITH PEAS. SECOND SERIES.

Statistics of Seed, Solutions, Planting, etc.

	Number of Experiment.	Date of Planting.	Weight of Sand.	Number of Seeds.	Weight of Seeds.	Amounts of Solutions added (one-half each March 30, the rest May 29.)*						Amount of Water Added.
						NI.	NIII.	P_2O_5.	Mg.	Fe.	Total.	
			kilos		grams.	cc.	cc.	cc.	cc.	cc.	cc.	cc.
Group I. Smaller Nitrogen Ration.	1	March 30	1	3	0.8707	...	50	30	20	1	101	2599
	3	" "	1	6	1.7237	...	50	30	20	1	101	2599
	5	" "	2	3	0.8117	...	50	30	20	1	101	2849
	7	" "	2	6	1.6973	...	50	30	20	1	101	2849
	9	" "	3	3	0.8379	...	50	30	20	1	101	3099
	11	" "	3	6	1.7219	...	50	30	20	1	101	3099
Group II. Larger Nitrogen Ration.	2	" "	1	3	0.8165	50	50	30	20	1	151	2574
	4	" "	1	6	1.7849	50	50	30	20	1	151	2574
	6	" "	2	3	0.8258	50	50	30	20	1	151	2824
	8	" "	2	6	1.6685	50	50	30	20	1	151	2824
	10	" "	3	3	0.8214	50	50	30	20	1	151	3074
	12	" "	3	6	1.6337	50	50	30	20	1	151	3074

	Number of Experiment.	Date of Harvesting.	Number of Matured Plants.	Average Height of Plants.	Number of Pods.	Number of Perfect Peas.	Number of Rudimentary Peas.	Weight of Vines, Foliage and Fruit.	Weight of Roots and Adhering Sand.	Total Weight of Plants and Adhering Sand.
				cm.				grams.	grams.	grams.
Group I. Smaller Nitrogen Ration.	1	July 3	3	40	5	12	4	5.5	12.9	18.4
	3	" "	6	38	10	18	4	6.8	4.9	11.7
	5	" "	3	45	7	17	6	7.0	17.7	24.7
	7	" "	6	35	12	15	8	6.4	21.4	27.8
	9	" "	3	49	7	23	1	7.3	19.0	26.3
	11	" "	6	38	14	23	6	8.8	24.2	33.0
Group II. Larger Nitrogen Ration.	2	" "	3	50	8	19	6	6.8	5.2	12.0
	4	" "	6	62	12	23	5	8.0	5.5	13.5
	6	" "	3	40	7	20	4	6.9	19.4	26.3
	8	" "	6	33	12	20	7	7.6	17.4	25.0
	10	" "	3	50	7	18	2	7.4	19.6	27.0
	12	" "	6†	45	9	15	6	8.0	10.7	18.7

* Except that the whole of solution "Fe" was added March 30.

† Only five plants matured.

Nitrogen Statistics.

	Number of Experiment.	Nitrogen supplied at beginning and during Experiment.			Nitrogen found at End of Experiment.			Gain + or Loss — of Nitrogen.
		In Seeds.	In Solutions.	Total.	In Vines, Roots, etc.	In Residual Solutions.	Total.	
		mgm.	mgm.	mgm.	mgm.	mgm.	mgm.	mgm.
Group I. Smaller Nitrogen Ration.	1	36.7	59.4	96.1	116.4	1.4	117.8	+ 21.7
	3	72.6	59.4	132.0	158.9	3.8	162.7	+ 30.7
	5	34.2	59.4	93.6	156.1	0.0	156.1	+ 62.5
	7	71.5	59.4	130.9	158.1	0.0	158.1	+ 27.2
	9	35.3	59.4	94.7	186.5	1.4	187.9	+ 93.2
	11	72.5	59.4	131.9	210.9	2.7	213.6	+ 81.7
Group II. Larger Nitrogen Ration.	2	34.4	136.9	171.3	178.9	2.0	180.9	+ 9.6
	4	75.2	136.9	212.1	200.6	12.8	213.4	+ 1.3
	6	34.8	136.9	171.7	149.6	1.2	150.8	— 20.9
	8	70.3	136.9	207.2	197.5	12.7	210.2	+ 3.0
	10	34.6	136.9	171.5	277.8	35.7	313.5	+ 142.0
	12	68.8	136.9	205.7	260.2	45.7	305.9	+ 100.2

Concerning the data in Table II the following statements may be made:

1. The seeds were planted March 30th, and the plants harvested July 3d. The plants were ripe, however, and watering ceased some time before the harvesting could be done, so that I do not think the actual period of active growth should be taken at over 72 days.

2. As three kilograms of sand held more solution than one, while the amounts of dissolved salts were the same, the concentration of the solutions differed widely. The amounts in each case varied somewhat with evaporation and watering. The solutions in the 3 kilos of sand contained generally from 0.8 to 1.6 grams, or thereabouts, of dissolved salts in 1000 cc. and were thus tolerably dilute. Those in 1 and 2 kilos of sand contained from 2.5 to 6 parts of salts per 1000, and were hence very concentrated. It has been shown by Nobbe[1] and others that though many of our cultivated plants may endure very concentrated solutions, yet if the concentration be sufficiently great or protracted, assimilation may be hindered and the development of the plants retarded or stopped. Thus Nobbe and Siegert found a concentration of 3 or even 2 per mille, *i. e.* 3 or 2 parts of salts in 1000 of solution, prejudicial to the growth of buckwheat and barley plants; and the general result of experiments on the growth of these plants in aqueous solutions indicates that a concentration of 1 per mille is

[1] Landw. Vs. Stationen, **6**, 17, and **8**, 337.

perhaps the most favorable to normal growth. A still greater dilution has, I believe, been found requisite for some leguminous plants. Accordingly we have in Nos. 1 to 8 a concentration unfavorable, and in Nos. 9 to 12 one tolerably well adapted to normal growth.

3. The amount of food in the solutions was estimated to be rather small for three plants, and made of course a very scanty supply for six. Accordingly Nos. 3, 4, 7, 8, 11 and 12 were very insufficiently, and Nos. 1, 2, 5, 6, 9 and 10 tolerably well fed.

4. The amounts of mineral food were the same for all. "The larger nitrogen ration" was calculated to supply an amount of nitrogen rather small in proportion to the mineral food, 140 mgms. in each case. "The smaller nitrogen ration" contained less than half as much nitrogen, 60 mgms. in each case.

We have thus, in the experiments of the Second Series, the variations in concentration of solutions, total food-supply, and supply of nitrogen, referred to above, as provided to test the effects of normal and abnormal conditions upon the assimilation of nitrogen.

We may place the principal data of Tables I and II together in such a way as to show more clearly the amounts of nitrogen supplied and found, as is done in Table III.

TABLE III.—NITROGEN STATISTICS OF THE EXPERIMENTS.

		Number of Experiment.	Kilos of Sand used.	Number of Plants.	Nitrogen supplied to Plants by Solution and Seed.*	Nitrogen contained in Plants	Gain +, or Loss — of Nitrogen, *i. e.* excess in Plant above that supplied by Solution and Seed.		
							Total Gain or Loss.	Gain or Loss in per cent.	
								Of Nitrogen supplied by Solution and Seed.	Of Nitrogen contained in Plants.
					mgm	mgm.	mgm.	per cent.	per cent.
	First Series.	A	2½	6	103.7	167.2	+ 63.5	+ 61.2	+ 38.0
		B	2½	4	120.6	133.8	+ 13.2	+ 10.9	+ 9.9
		C	2½	4	95.7	108.7	+ 13.0	+ 13.6	+ 12.0
Second Series.	Group I. Smaller Nitrogen Ration.	1	1	3	94.7	116.4	+ 21.7	+ 22.9	+ 18.6
		3	1	6	128.2	158.9	+ 30.7	+ 23.9	+ 19.3
		5	2	3	93.6	156.1	+ 62.5	+ 66.8	+ 40.0
		7	2	6	130.9	158.1	+ 27.2	+ 20.8	+ 17.2
		9	3	3	93.3	186.5	+ 93.2	+ 99.9	+ 50.0
		11	3	6	129.2	210.9	+ 81.7	+ 63.2	+ 38.7
	Group II. Larger Nitrogen Ration.	2	1	3	169.3	178.9	+ 9.6	+ 5.6	+ 5.4
		4	1	6	199.3	200.6	+ 1.3	+ 5.7	+ 5.6
		6	2	3	170.5	149.6	− 20.9	− 12.3	− 14.0
		8	2	6	194.5	197.5	+ 3.0	+ 1.5	+ 1.5
		10	3	3	135.8	277.5	+ 142.0	+ 104.5	+ 51.1
		12	3	6	161.0	260.2	+ 99.2	+ 62.0	+ 38.1

*Computed by adding the nitrogen of nutritive solution and seed, and subtracting that of residual solution. This is subtracted from the nitrogen in the plants, and the difference called "Gain or Loss." Any loss of nitrogen during the experiment, by decomposition or otherwise, would thus diminish the calculated gain of nitrogen.

Results of the Experiments.

Of eight trials in concentrated solutions, Nos. 1–8, one showed a small loss, and the rest more or less gain of nitrogen. I do not know how to explain the loss of nitrogen, unless it be by decomposition of either the nitrates in the presence of germinating seeds, as shown by Boussingault (see above), or the nitrogenous compounds of the seeds, or both. If such decomposition took place, it may, for aught I can say, have occurred in the dilute solutions also.

In the moderately dilute solutions, Nos. 8–12, in which the concentration was such as has elsewhere been found favorable to healthy growth, the nitrogen of the plants largely exceeded that furnished by nutritive solution and seed. This appears more clearly when the figures are arranged as below.

Atmospheric Nitrogen Acquired by Plants Grown in Moderately Dilute Solutions.

	Gain of Nitrogen.			
	In Milligrams per Experiment.		In per cent. of Total Nitrogen of Plants.	
	With smaller Nitrogen Ration.	With larger Nitrogen Ration.	With smaller Nitrogen Ration.	With larger Nitrogen Ration.
With six plants, *i. e.* smaller food supply..	81.7 mgms.	99.2 mgms.	38.7 per ct.	38.1 per ct.
With three plants, *i. e.* larger food supply..	93.2 "	142.0 "	50.0 "	51.1 "

That is to say, in the four trials with solutions sufficiently dilute to permit normal assimilation, the very poorly-fed plants obtained over one-third, and the tolerably well-fed ones one-half of their whole nitrogen from the atmosphere. The plants acquired a milligram of nitrogen from the air, for every milligram taken from solution and seed. And what is even more noticeable, they did this, not only where the amount of nitrogen supplied was very small, but also where it was more than twice as large.

As stated elsewhere, the apparent sources of error were all such as to diminish the nitrogen found at the end of the experiment. The apparent gain of nitrogen therefore could have been no more, and may have been less than the actual gain. Furthermore, the food-supply, even in the most favorable cases, was evidently smaller than the plants needed for their best development, since

even the best-fed plants appeared rather stunted. In later trials made to test this special question of the effect of food-supply, peas were supplied with solutions of the same composition and concentration as those which gave the best results above, but in much larger quantity. The result of this larger food-supply was a much more vigorous growth. The natural inference is, that if the peas which had the largest supply of food and acquired the most nitrogen from the air had been still better fed, they might have assimilated as much or more atmospheric nitrogen.

As regards the effects of the three factors, concentration of nutritive solution, total food supply, and supply of nitrogen, the results show very clearly that the assimilation of nitrogen decreased as each was made abnormal, and increased as each became more nearly normal.

The quantity of nitrogen acquired from the atmosphere appears still more strikingly if we compare it with the quantities contained in plants as commonly cultivated. The superficial area of the pots in which these plants grew was about 104 square centimetres. Remembering that one miligram per square decimetre corresponds to one kilogram per hectare, and 1.12 kilos per hectare to 1 pound per acre, and taking for the average percentages of nitrogen in field crops those given in Wolff's tables (Mentzel und V. Lengerke, Landw. Kalender, 1884), we have the following figures:

COMPARISON BETWEEN THE AMOUNTS OF ATMOSPHERIC NITROGEN ACQUIRED BY THE EXPERIMENTAL PLANTS AND THE TOTAL NITROGEN OF PLANTS IN ORDINARY CULTURE.

	Nitrogen.					
	Per experiment.		Per hectare.		Per acre.	
	Contained in Plants.	Acquired from Air by Plants.	Contained in Plants.	Acquired from Air by Plants.	Contained in Plants.	Acquired from Air by Plants.
Plants in Dilute Solutions.	mgm.	mgm.	kilos.	kilos.	lbs.	lbs.
Smaller nitrogen ration. { Smaller food supply	210.9	81.7	202.9	78.6	181.4	70.3
Larger total food supply.	186.5	93.2	179.4	89.7	160.4	80.2
Larger nitrogen ration. { Smaller food supply	260.2	99.2	250.3	95.4	223.8	85.3
Larger food supply	277.8	142.0	267.2	136.6	238.9	122.1
Average of experiments with dilute solutions	233.9	104.0	225.0	100.0	201.1	89.5
Plants in Field Culture.						
Wheat, 30 bushels (1800 lbs.) per acre			66.1		59.0	
Hay (mixed grasses), 5000 lbs. per acre			86.8		77.5	
Clover hay, 6000 lbs. per acre			132.8		118.6	

In the experiments in which the conditions of growth were approximately normal, the excess of nitrogen in the plant over that supplied by nutritive solution and seed averaged 90 pounds per acre or 100 kilos per hectare; while in the single one where there was no considerable apparent hindrance to normal growth, that with three plants and the larger nitrogen ration, it rose to 122.1 pounds per acre, or 136.6 kilos per hectare, twice as much as the total nitrogen in grain and straw of a wheat crop of thirty bushels, and more than the total nitrogen of three tons of clover hay. And this remarkable gain cannot represent more, and may be less, than the actual quantity of atmospheric nitrogen which the plants acquired during their brief period of seventy-two days of growth.

Discussion of the Results.

This nitrogen must have been either absorbed by the foliage of the plants, or first taken from the air by the nutritive solutions, and thus communicated to the plants through their roots. If it came by the latter route, it was probably as combined nitrogen, ammonia, nitrates or nitrites.

Was the atmospheric nitrogen absorbed directly by the foliage of the plants, or was it first absorbed by the nutritive solutions and thus communicated to the plants through their roots?

In order to eliminate the uncertain factor of absorption of nitrogen compounds through the roots of the plants, a series of experiments was devised to admit only air freed from nitrogen compounds to contact with the nutritive solutions, the foliage remaining in open air. These unfortunately failed of completion, and I have since found no opportunity to repeat them, though I hope hereafter to do so.

During the course of the experiments of the second series, a number of pots with sand and solutions like those in which the plants grew were kept alongside the latter. The solutions at the end of the experiments revealed only such minute quantities of combined nitrogen as are commonly found in natural waters exposed to the air. That these solutions, without plants, had so little of nitrogen compounds, is, however, no proof that the solutions in which the plants grew might not have yielded to the plants some of the ammonia which they were continually absorbing, and

which, if not somehow seized upon, would escape by virtue of its tension. The fact that the solutions in which the plants grew were neutral or faintly alkaline, would, however, make the hypothesis of any considerable absorption of ammonia apparently improbable. It is worth noting, too, that the residual solutions at the end of the experiment contained only the minutest quantities of ammonia discernible by aid of Nessler's reagent.

The only experiments with which I am familiar, bearing directly upon this problem, are those of Heinrichs[1] and Schlössing.[2] These were made to determine the maximum amounts of combined nitrogen which could be absorbed from the atmosphere under the most favorable circumstances. Heinrichs exposed dilute acid, and Schlössing a moist, acid, porous soil to the air, protecting them, however, from rain and dew. Heinrichs' experiments continued through two years; Schlössing's during shorter periods in the summer months. The absorption of atmospheric nitrogen was greatest in summer and least in winter. For the period of my experiments, 72 days in April, May and June, according to my computation, the amount of nitrogen absorbed as ammonia by dilute acid was practically identical with that absorbed as ammonia, and nitric and nitrous acids by the soil, to wit, 9.8 mgms. per square decimetre (kilos per hectare); but the amounts of nitric and nitrous acids in the atmosphere are very small, and, as has been noted, especially by Schlössing, these are brought to the earth by rain and other aqueous deposits, from which ammonia, by virtue of its tension, more readily escapes and is thus left in the air. Schlössing determined, furthermore, the nitric and nitrous acids as well as the ammonia absorbed.

The solution in which my plants grew was, like the soil and acid solutions above, protected from rain and dew, and was neutral or faintly alkaline. It would seem that they could hardly have absorbed as much of nitrogen compounds from the air as an acid solution. That they could have both absorbed and communicated to the plants so much combined nitrogen is still harder to believe. But allowing that the plants in these experiments could have obtained in this way as much nitrogen as was absorbed by the acid solutions or soil in the experiments of Heinrichs and Schlössing, to wit, 10 kilos per hectare, we should even then have, in the case in which

[1] Forschungen a. d. Geb. d. Agrikulturphysik, **4**, 446. [2] Compt. rend. **82**, 1105.

the growth appears to have been most nearly normal, that with three plants, in the dilute solution, with the larger nitrogen ration:

Minimum amount of atmospheric nitrogen acquired by plants, ...	137	kilos per hectare.
Maximum amount of atmospheric nitrogen conveyed to plants by solution, . .	10	" "
Balance, minimum acquired by foliage, .	127	" "
Balance in per cent. of total atmospheric nitrogen, ...	93	per cent.
Balance in per cent. of total nitrogen of plants, ...	47	"

That is to say, if it be correct to assume that the neutral or faintly alkaline nutritive solutions here could have been absorbed from the air and communicated to the roots no more nitrogen than the maximum amount found to be absorbed elsewhere under the most favorable conditions for absorption, namely, by an acid solution, or a moist, acid, porous soil, we have, in the case in which the conditions of assimilation were most nearly normal, an amount of nitrogen in the plants which they could have obtained from no other source than the atmosphere, and through no other channel than their foliage, and which could not have been less, and was probably more than 47 per cent. of the total nitrogen of the plant, and corresponded to 127 kilos per hectare (113 pounds per acre).

Was the atmospheric nitrogen acquired by the plants in the form of combined nitrogen?

If this nitrogen was acquired by the foliage, it must have been either free or combined nitrogen. The supposition that the plants could have acquired so much combined nitrogen from the air would seem to me very improbable.

The theory has been proposed by Grandeau[1] that the leaf, containing acid juices, "acts like an acid, watery medium, absorbing ammonia like an acid solution," and that plants may in this way acquire considerable quantities of combined nitrogen from the air. The amount of leaf surface of the plants in these experiments was not estimated. The plants were, however, small even for dwarf

[1] Nutrition de la Plante, pp. 574-578.

peas. In a later trial the area of the full-grown leaves in a duplicate of the experiment which gave the largest nitrogen assimilation, was computed at not over 320 cm. at the outside (assuming the surface to be smooth), which would make for the two surfaces 640 cm. or about six times the superficial area of the medium in which the plants grew. The maximum absorption of ammonia by an acid solution of this surface during the period of growth of the plants was computed above at a little less than the equivalent of 10 kilos of nitrogen per hectare. If, now, we assume that the tissues enclosing the juices offer no resistance to the passage of ammonia, and that the leaf acts as an "acid, watery medium, absorbing ammonia like an acidified solution," and if we go still further, and allow the absorption to have been as great during the whole period of growth as would correspond to the double surface of the full-grown leaves; and if, finally, we allow this absorption to be equivalent to the maximum observed elsewhere, we should, even then, have an absorption equivalent to only 60 kilos per hectare, which, added to the maximum possible absorption for the solution as above estimated, would make only 70 kilos, while the plants somehow acquired a minimum of 137 kilos per hectare.

But the best information at hand[1] forbids the assumption that the juices are uniformly or even generally acid; of the permeability of the leaf tissues to gases we have little certain knowledge; the leaves had their full size during only the latter part of the period of growth; in short, it would require a considerable stretch of the imagination to assume any such absorption as that just calculated. Crude and unreliable as these estimates are, they nevertheless make it very difficult to conceive how such very large quantities of nitrogen as these plants obtained could have been absorbed as nitrogen compounds by their foliage from the air.

Of course, the amount of combined nitrogen which the plants could have obtained in this way is a matter to be settled by experiment, and the considerations just presented may be superfluous. Instead of urging any views of my own, therefore, I may with greater propriety cite those of more experienced investigators.

M. Boussingault, in discussing[2] the sources of the nitrogen of plants, says that "Part of the nitrogen of plants comes from the

[1] *E. g. vid.* Sachs Botanische Zeitung, 1862, 257.

[2] In a communication to Dr. J. H. Gilbert, *vide* paper "On some points connected with vegetation," Am. Jour. Sci. [3], **13**, 183 (reprinted from Address delivered at South Kensington).

atmosphere, because it furnishes ammonia in the form of carbonate, nitrates or nitrites, and various kinds of dust. Theodore de Saussure was first to demonstrate the presence of ammonia in the air, and, consequently, in meteoric waters. Liebig exaggerated the influence of this ammonia on vegetation, since he went so far as to deny the utility of the nitrogen which forms a part of farm-yard manure. This influence is, nevertheless, real and comprised within limits, which have recently been indicated in the remarkable investigations of M. Schlössing."

Messrs. Lawes and Gilbert, in an extended discussion of this subject, remark as follows[1] (the italics are my own):

"One view which has been advocated is, that broad-leaved plants have the power of taking up combined nitrogen from the atmosphere, in a manner or in a degree not possessed by the narrow-leaved, gramineous plants. The only experiments that we are aware of, made to determine whether plants can take up nitrogen by their leaves from ammonia supplied to them in the ambient atmosphere, are those of Adolph Mayer[2] in Germany, and of Schlössing[3] in France. Both found that very small quantities of nitrogen were so taken up; but both concluded that the action takes place in very immaterial degree in natural vegetation. We have elsewhere shown that not only a consideration of the chemistry and the physics of the subject would lead to the conclusion that the plants which assimilate more nitrogen over a given area than others, do not do so by virtue of a greater power of absorbing already combined nitrogen from the atmosphere, by their leaves; but apart from such considerations, our statistics of nitrogen production *seem to preclude the idea that the broad-leaved root crops, turnips and the like, to which the function has with the most confidence been attributed, take up any material proportion of their nitrogen by their leaves from combined nitrogen in the atmosphere.*"

[1] "Determination of Nitrogen Soils," London Edition, p. 21.

[2] It is, nevertheless, worth noting that in Mayer's experiments (Landw. Vs. Stationen, **17**, 359), the plants had for the most part little or no nitrogen at the disposal of their roots, except that supplied by the seed, that the other conditions of growth were more or less abnormal, and that in consequence the plants were stunted and sickly. While therefore they render Mayer's conclusion probable, they do not seem to me decisive.

[3] The experiments of Schlössing I presume to be those described in the *Comptes rendus*, **78**, 1700. These were made with tobacco plants grown with the roots in a fertile soil, but with the foliage enclosed in a glass case, the air in which was artificially supplied with a very large amount of ammonia. The results show the possibility of the absorption of ammonia by the foliage, but seem to me to give very little certain indication as to the amount that may be acquired by plants under normal conditions.

And further, in recapitulating the results of their own and other experiments upon the various supposed sources of nitrogen of crops, Messrs. Lawes and Gilbert continue:[1]

"It has been shown that the determined amounts of combined nitrogen annually coming down in the measured aqueous deposits from the atmosphere in the open country are entirely insufficient to do more than supply a small proportion of the nitrogen assimilated by crops so grown.

"With regard to other possible supplies of already combined nitrogen from the atmosphere to the soil, it has been pointed out that there is no quantitive evidence whatever at command, and that such evidence as does exist leads to the conclusion that such supplies are *very limited and inadequate.*

"*The same may be said, even in a greater degree,* of the supposed combination of the free nitrogen of the air within the soil; also *of the supposition that plants take up any material proportion of their nitrogen from combined nitrogen in the atmosphere by their leaves.*"

There is no doubt that plants do obtain some combined nitrogen from the atmosphere. But unless the decided conclusions of those who have devoted the most experimental study to the subject, as well as my own estimates above, are very far out of the way, the supposition that the plants, in the experiments here reported, could have acquired more than a fraction of their atmospheric nitrogen in this manner, would be out of the question.

Did the plants acquire free nitrogen from the atmosphere?

The only other possible hypothesis is that the plants assimilated the free nitrogen of the air. That plants assimilate free nitrogen is contrary to general belief and to the results of the best investigations of the subject. The disagreement between these results and my own may, however, be more apparent than real. Two points in particular seem to me worthy of note.

First. The plants in the experiments in which no considerable assimilation of atmospheric nitrogen has been observed had, in general, little or no combined nitrogen at the disposal of their roots save the small quantities contained in the seed. The depression of nitrogen assimilation consequent upon inadequate supply of food, especially of nitrogen, in my experiments is very marked.

[1] *Loc. cit.* p. 30.

Second. The experiments which are most decisive against the assimilation of free nitrogen, namely, those of Boussingault[1] and of Lawes, Gilbert and Pugh,[2] were conducted under glass covers connected with the earth. Berthelot has shown that free nitrogen may be assimilated by vegetable substances, dextrine, cellulose, etc., under the influence of electricity of a potential similar to that which obtains near the surface of the earth, in the strata of air in which our cultivated plants grow.[3] The inference that the compounds in living plants may assimilate nitrogen in the same way is natural. That this electrical tension may have been absent in the experiments with the plants under glass, referred to, would seem probable. The hypothesis of the assimilation of free nitrogen by plants through the agency of electricity, and the absence of that agency in the experiments of Boussingault and of Lawes, Gilbert and Pugh, would, with the effect of scanty food supply, explain the discrepancy between their experiments and my own, in which the conditions of growth were normal, and would clear up the worst difficulty in the much vexed question of the sources of nitrogen of plants.

Of course such hypotheses can be accepted only after experimental verification. I hope that circumstances may permit the execution of some experiments which have been planned for the study of this and some of the other phases of the question.

In this connection it may not be out of place to note the observation made by Lawes and Gilbert,[4] Dehérain[5] and Schulz-Lupitz,[6] that while soils in which potatoes, cereals, and other crops were cultivated grew poorer in nitrogen, the nitrogen in those on which legumes were grown, under conditions precisely similar, uniformly increased. That is to say, the leguminous plants after providing themselves with their larger amounts of nitrogen, left more nitrogen in the soil than the latter contained before. While the explanation of this fact is, doubtless, complex, and very likely involves an acquisition of nitrogen by the soil from the air, as combined nitrogen, and perhaps as free nitrogen fixed by the humus of the soil through the agency of electricity; yet it seems to me not improbable that a most important factor must be sought in a power of the plants to acquire nitrogen from the air, in which some of the legumes especially excel.

[1] Ann. ch. Phys. 1838-1855, passim.
[2] Phil. Trans. 1861, **2**, 437.
[3] Compt. rend. 82–88, passim, and in more detail in Ann. ch. Phys. [5] **10**, 52, and **12**, 457.
[4] Am. Jour. Sci. [3] **13**, 28. [5] Ann. Agronom., 1882, 322. [6] Ct. bt. f. Ag. Chem., 1883, 145.

In Conclusion.

The outcome of these experiments may be concisely stated thus:

1. The plants, peas, grown in nutritive solutions exposed to the air, but protected from rain and dew, contained at maturity much more nitrogen than was supplied them in nutritive solution and seed. Such were the results of a first series of trials, confirmed, even more strikingly, by a second series the succeeding year. For this excess of nitrogen there was but one possible source, namely, the atmosphere.

2. The conditions of growth were varied by varying (1) the concentration of the nutritive solutions, (2) the total amount of food, and (3) the amount of nitrogen in the nutritive solutions. In each case the gain of nitrogen was largest when the conditions of growth were most nearly normal, and smaller as either condition was made abnormal. Thus the gain was small where the solutions were very concentrated, and largest where the concentration was such as has generally been found favorable to normal assimilation and growth. The amount of nitrogen acquired from the atmosphere rose and fell with the amount of food at the disposal of the roots, being largest where the plants were tolerably well fed, and smallest where the food-supply was inadequate. So, likewise, where the supply of nitrogen varied, the amount of mineral food remaining the same, the plants acquired more or less aerial nitrogen in proportion as more or less nitrogen was supplied to them in the nutritive solution.

3. In the four trials with solutions sufficiently dilute to permit normal assimilation, the very poorly fed plants obtained one-third, and the tolerably well fed ones one-half of their whole nitrogen from the air. And what is even more noticeable, they did this not only where the quantity of nitrogen in the nutritive solution and seed was very small, but also where it was more than twice as large. When we compare the nitrogen in the experimental plants with that in plants commonly cultivated, by comparing the area of the pots in which the experimental plants grew with an acre or a hectare, it appears that, in the case in which the conditions of growth were most nearly normal, the plants acquired atmospheric nitrogen at the rate of 137 kilograms per hectare, or 122 pounds per acre, more than twice as much as the total amount contained in the grain and straw of a wheat crop of thirty bushels of grain

per acre (27 hectolitres per hectare), and more than is contained in a clover crop of 6000 pounds per acre (6720 kilos per hectare).

5. How, and in what form, this nitrogen was acquired the experiments do not tell. It must have come to the plants as either combined nitrogen, ammonia, nitric acid or nitrous acid, or as free nitrogen. It must have been either taken directly by the foliage, or first absorbed by the nutritive solution and communicated by it to roots. That the whole, or indeed any considerable portion could have been gathered from the air and conveyed to the plants by the nutritive solution, which was neutral or slightly alkaline during growth, is, to say the least, in the most direct apparent contradiction with the best experimental evidence at hand. The hypothesis of the absorption of any considerable quantity of combined nitrogen by the leaves of the plants is directly opposed, as well to the testimony of the most reliable experiments upon the subject as to the seemingly unanimous opinion of the men who have made them. The only remaining hypothesis is that of the assimilation of the free nitrogen of the air by the plants. This is likewise contrary to the results of the best investigations.

A way out of the difficulty may, perhaps, be found in the observation by Berthelot of the assimilation of free nitrogen by vegetable matters, through aid of electricity of a potential similar to that which obtains in the air near the surface of the earth; an agency which may have been excluded in the experiments which are most decisive against the assimilation of free nitrogen.

As to whether this latter hypothesis, or either of the others, is correct, I venture no opinion, deeming it wiser to abide by the simple fact that the plants acquired a considerable quantity of nitrogen from the atmosphere, and look to future research for the explanation.

I improve this opportunity to express my obligations to my assistant, Mr. C. D. Woods, by whom the details of the experiments above described have been most faithfully and skilfully performed.

It gives me great pleasure, also, to bear testimony to the generosity of Hon. J. W. Alsop, M. D., of this city (Middletown, Conn.), who has, by defraying the larger part of the pecuniary cost, and by aid in other ways, made the investigations practicable.

Chemical Laboratory, Wesleyan University.

Appendix.

The following are details of the chemical work of the experiments. It may not be out of place to say that the nitrogen determinations were made after a not inconsiderable outlay of time and labor in getting the methods well in hand.

The sand was washed with ordinary, and then with distilled water, ignited, and finally tested for nitrogen compounds by combustion with soda-lime, which revealed no nitrogen.

The water used for the solutions, for watering the plants, and for separating roots and residual solutions from sand at the end of the experiment, had been previously freed from nitrogen compounds by distilling with potassium permanganate and hydroxide, and rejecting so much of the distillate as gave a visible ammonia reaction with Nessler's reagent.

The determinations of nitrogen in the seeds and plants were made by the soda-lime method. Those of the nitrogen in the nutritive solutions employed, and in the residual solutions at the end of the experiment, were made by the method of Schulze-Tiemann.[1]

It is quite possible that the plants may have contained nitrates, more or less of the nitrogen of which would escape determination by soda-lime. The error thus introduced, if any, would decrease the amount of nitrogen found at the end of the experiment, and thus the apparent gain of nitrogen from the air.

Nitrogen in Peas. Determined by Soda-lime.

First Series. Five peas. Nitrogen determined in each separately.

	Weight of pea.	N. Found.	Per cent. N.	
No. 1	217.4 mgm.	6.96 mgm.	3.20	
" 2	238.7	7.83	3.28	Average, 3.334 per cent. N.
" 3	215.0	7.32	3.40	
" 4	206.9	6.96	3.36	
" 5	234.0	8.03	3.43	

Second Series. Several peas ground together, and determinations made in three separate portions of this sample.

Weight of portion.	N. Found.	Per cent. N.	
1000 mgm.	42.18 mgm.	4.22	Average, 4.21 per cent. N.
1000	42.18	4.22	
1000	42.02	4.20	

[1] Kubel-Tiemann, *Untersuchung von Wasser*, Braunschweig, 1874, 55; also Fres. Quant. Anal., Johnson and Allen, N. Y., 1883, 473.

Nitrogen in Plants. Determined by Soda-lime.

First Series.

	Vines, roots, etc.[1] mgm.	N. found. mgm.	Per cent. N.	
A	1103	15.42	1.398	Average,
	1000	14.36	1.436	1.417 per ct.
	1000	14.08	1.408	

Total vines, roots, etc. = 11.8 gram @ 1.417 per cent. = 167.21 mgm. N.

B	1000	12.17	1.217	Average,
	1000	12.17	1.217	1.217 per ct.
	1000	12.17	1.217	

Total vines, roots, etc. = 11.0 gram @ 1.217 per cent. = 133.87 mgm. N.

	Vines, roots, etc. mgm.	N. found. mgm.	Per cent. N.	
C	1000	5.78	0.578	Average,
	1000	5.78	0.578	0.578 per ct.
	1000	5.78	0.578	

Total vines, roots, etc. = 18.8 gram @ 0.578 per cent. = 108.70 mgm. N.

D	1000	8.06	0.806	Average
	1000	8.06	0 806	0.812 per ct.
	1000	8 24	0.824	

Total vines, roots, etc. = 11.6 gram @ 0.812 per cent. = 94.19 mgm. N.

E	1000 mgm.	8.22 mgm.	0.822	Average,
	1000	8.06	0.806	0.817 per cent.
	1000	8.22	0.822	

Total vines, roots, etc. = 10.1 gram @ 0.817 per cent. = 82.52 mgm. N.

Second Series.

	Wt. vines, roots, etc. mgm.	N. found. mgm.	Per cent N.	
1	1000	63.60	6.36	Average,
	1000	63.00	6.30	6.33 per ct.

Total vines, roots, etc. = 18.4 gram @ 6.33 per cent. = 116.45 mgm. N.

3	1000	135 8	13.58	Average,
	1000	135 8	13.58	13.58 per ct.

Total vines, roots, etc. = 11.7 gram @ 13.58 per cent. = 158.90 mgm. N.

5	1000	63.60	6.36	Average,
	1000	62.80	6.28	6.32 per ct.

Total vines, roots, etc. = 24.7 gram @ 6.32 per cent. = 156.10 mgm. N.

7	1000	56.9	5.69	Average,
	1000	56.9	5.69	5.69 per ct.

Total vines, roots, etc. = 27.8 gram @ 5.69 per cent. = 158.1 mgm. N.

9	1000	71.2	7.12	Average,
	1000	70.6	7.06	7.09 per ct.

Total vines, roots, etc. = 26.3 gram @ 7.09 per cent. = 186.5 mgm. N.

11	1000	64.2	6.42	Average,
	1000	63.6	6.36	6.39 per ct.

Total vines, roots, etc. = 33.0 gram @ 6.39 per cent. = 210.9 mgm. N.

	Wt. vines, roots, etc. mgm.	N. found. mgm.	Per cent. N.	
2	1000	149 4	14.94	Average,
	1000	148 7	14.87	14.91 per ct.

Total vines, roots, etc. = 12 gram @ 14.91 per cent. = 178.92 mgm. N.

4	1000	148.7	14.87	Average,
	1000	148.4	14.84	14.86 per ct.

Total vines, roots, etc. = 13.5 gram @ 14.86 per cent. = 200.62 mgm. N.

6	1000	56.9	5.69	Average,
	1000	56.9	5.69	5.69 per ct.

Total vines, roots, etc. = 26.3 gram @ 5.69 per cent. = 149.6 mgm. N.

8	1000	79.0	7.90	Average,
	1000	79.0	7 90	7.90 per ct.

Total vines, roots, etc. = 25.0 gram @ 7.90 per cent. = 197.50 mgm. N.

10	1000	103.2	10.32	Average,
	1000	102.6	10.26	10.29 per ct.

Total vines, roots, etc. = 27. gram @ 10.29 per cent. = 277.80 mgm. N.

12	1000	139.2	13.92	Average,
	1000	139 2	13 92	13.92 per ct.

Total vines, roots, etc. = 18.7 gram @ 13.92 per cent. = 260.22 mgm. N.

Nitrogen in Nutritive Solutions determined, like that in Residual Solutions, by Method of Schulze-Tiemann.

First Series

Solution I.	Solution II.	N. found.
12 cc. +	12 cc.	18.45 mgm.
12 cc.		0.00831 mgm. 18.40 "
	12 cc.	0.01009 "
12 cc. +	12 cc.	18.43 "
12 cc. +	12 cc.	18.43 "

Average of 24 cc. of solutions (12 cc. each) I and II, 18.43 "

[1] The weights include that of sand which adhered to the roots in varying proportions, and which thus accounts for the wide variations in the percentages of nitrogen.

SECOND SERIES.

Solution NI.	
Solution.	N. found.
25 cc.	38.84 mgm.
25 cc.	38.70 "
25 cc.	38.70 "
Average 1 cc. Solution = 1.5499 mgm. N.	

Solution NIII.	
Solution.	N. found.
25 cc.	29.81 mgm.
25 cc.	29.61 "
25 cc.	29.76 "
25 cc.	29.70 "
Average 1 cc. Solution = 1.1888 mgm. N.	

Nitrogen in Residual Solutions at End of Experiments.

FIRST SERIES.

	Solution.	Nitrogen found.
A	½ of extract.	3.579 mgm.
	½ "	3.597
	Total.....	7.176
B	3-7 of extract.	3.217 mgm.
	4-7 "	4.744
	Total...	7.961

	Solution.	Nitrogen found.
C	½ of extract.	0.651 mgm.
	⅛ "	0.685
	Total.....	1.336
D	4-5 of extract.	2.580 mgm.
	Total (calculated)....	3.096

	Solution.	Nitrogen found.
E	½ extract.	28.542 mgm.
	⅓ "	18.803
	1/6 "	9.474
	Total.....	56.819

SECOND SERIES.

	Solution.	Nitrogen found.
1	½ extract.	0.683 mgm.
	½ "	0.683
	Total.....	1.366
3	¼ extract.	0.939 mgm.
	¼ "	0.938
	Total (calculated)....	3.754
5	No nitrates in extract.	
7	No nitrates in extract.	
9	½ extract.	0.719 mgm.
	½ "	0.719
	Total	1.438
11	⅓ extract.	0.88 mgm.
	⅓ "	0.92
	Total (calculated).....	2.70

	Solution.	Nitrogen found.
2	½ extract.	0 993 mgm.
	½ "	0.993
	Total.....	1.986
4	½ extract.	6 395 mgm.
	½ "	6.403
	Total.....	12.798
6	⅓ extract.	0.40 mgm.
	⅓ "	0.38
	Total (calculated)..	1.17
8	¼ extract.	3.16
	¼ "	3.18
	Total (calculated)..	12.68
10	⅓ extract.	11.87 mgm.
	⅓ "	11.91
	Total (calculated)..	35.68
12	⅓ extract.	14.88 mgm.
	⅓ "	14.91
	Total (calculated)..	44.69

I may also add that the residual solutions tested with Nessler's reagent were for ammonia, but revealed only traces.

To test the ease and completeness of removal of nitrates from sand by washing, as was done in separating the residual solution for determination of its nitrogen, the following trials were made with solutions which were put in sand and then washed with pure water. The smallness of the amount of water required for complete washing out of the nitrates, which has also been observed elsewhere, was here very noticeable.

Nitrogen in form of BaN_2O_6	Amount of sand.	NO in solution added to sand.	NO in extract from sand.
"	500 gram.	0.212 gram.	0.214 gram.
Solution I and II.	"	0.224	0.223
"	"	0.395	0.393
"	"	0.395	0.395
"	"	0.263	0.262
"	"	0.263	0.263

Contributions from the Chemical Bureau, U. S. Department of Agriculture.

III.[1]—THE CHEMICAL COMPOSITION OF THE PRODUCTS OF ROLLER MILLING OF WHEAT.

By Clifford Richardson.

The hard spring wheats, which have been mentioned in a previous paper as being rich in albuminoids, under the ordinary process of low milling furnish a dark colored flour of little value. To overcome this the roller mills have been introduced and the wheat is converted to flour by gradual reduction.

The number of products and by-products produced in roller mills is large, and the object of the investigation described in this paper was an examination and analysis of them all, for the purpose of ascertaining the composition of various portions of the grain and of the finished flours and other material derived therefrom.

The process, described very briefly, consists in preparing the wheat for the rolls, or breaks, as they are called, by the removal

[1] The articles beginning on pages 289 and 302 should have been numbered I and II in this series.

of foreign seed, dirt, chaff, and certain portions of the outer coatings of the grain with their adherent hairs; putting the cleaned grain through a series of rolls, after each of which all the reduced portion is removed and collected as chop, the coarse material being cleaned from all adherent matter and fed to the following roll until it comes from the last one as mere bran; purifying the various chops by appropriate machinery, which removes shorts, dusty particles, etc., and grades the coarser part, consisting of the interior or floury portion of the grain, into middlings of various sizes; purifications of these middlings from all foreign matter; reduction of the purified middlings between rolls or with stones, in the first manner flattening the germ so that it can be removed in the bolt; and mixing the graded flours for the market.

These are the chief points of the process. The re-purification of the middlings not reduced in the first operation of this character, and the collection of the lower grades of flour produced, incidental to the imperfections of the process, are additional details to be studied.

From this explanation the names of the products mentioned will be intelligible. For a complete understanding of the analyses, however, it will be necessary to consider the structure of the wheat grain and to know the portions of it which are represented in the different products. In my original report both these points have been explained at length. It will suffice here to say in regard to the first that the grain consists, essentially, of the floury portion, the endosperm, around which extends a continuation of the germ known as the embryous envelope. The germ itself is at one end of the grain and quite distinct from the endosperm. About all the previous parts extend the outer envelopes, consisting of five different layers, known as the cuticle, epicarp, endocarp, testa and tegmen. These, together with portions of the embryous envelope, make up the bran.

As has been said, the analyses will show that the composition of any product is dependent on the proportion of different parts of the grain found therein. In the following list there is given, therefore, the results of a physical examination of each one, and in it will be found the explanation of many of the results of the analyses.

PARTS OF THE WHEAT GRAIN IN DIFFERENT MILL PRODUCTS.

2001. *Wheat as it enters the mill.* The whole wheat grain mixed with cockle, oats, and other foreign seed, as it comes from the thrasher.

2002. *Wheat prepared for the rolls.* The foreign seeds have been removed with the exception of a few grains of cockle and oats. The cockle is therefore to be found in subsequent parts of the process. The hairs have been largely rubbed off, together with portions of the cuticle. Some hairs are, however, still left, and portions of the cuticle remain attached and semi-detached, especially toward the crease. The grain as a whole presents a changed and much cleaner appearance.

2003. *Cockle and screenings.* Among the foreign seeds there are found principally cockle and a species of polygonum and oats, together with broken pieces of wheat, dirt, chaff, etc.

2004. *Scourings removed by cleaners.* These consist almost entirely of cuticle and hairs, but portions of epicarp, with the hairs still adherent, and of endocarp are present. Treatment with iodine reveals a small amount of endosperm or starch, and shows the inner part of the outer coats of the grain is the most highly nitrogeneous. The contrast between the embryous membrane and endocarp, and the epicarp and cuticle is prominent. The embryous membrane is recognized by its roundish cells; the endocarp by its transverse cells, twice as long as broad, and packed closely and regularly, like cigars, which has given it the name of cigar coat, and the epicarp by its very long and irregular cells arranged longitudinally, the cuticle being of a similar sort.

2005. *First break.* The grain is split along the crease normally into two halves, but also frequently into fours, or even more irregularly. The glistening, hard, floury endosperm makes its appearance for the first time. Comparatively little flour or dust is made.

2006. *Chop from first break.* This consists principally of endosperm, but small portions of bran[1] and germ are present in the former, including all the various outer coats.

2007. *Second break.* In this break the greater part of the endosperm is separated from the bran, and is seen as large well-shapen middlings, together, of course, with some small stuff and dust.

[1] Bran is used in this description as denoting and including any part of the coats of the grain.

2008. *Chop from second break.* This is chiefly endosperm, with somewhat less bran than the previous chop. Whole germs and parts are numerous. The endosperm is of all sizes, but the greater portion of large angular fragments. The bran includes portions of all the outer coverings, while dusty matter and starch grains are quite abundant.

2009. *Third break.* The endosperm is so completely separated in this break that it only remains in scattered patches upon the bran, and the embryous membrane is quite visible.

2010. *Chop from third break.* The middling or particles of endosperm are much finer, and there is more dust. Small portions of germ are plentiful. The branny particles are similar in nature to those in the last chop, but smaller, and there is more dust of a nitrogeneous kind.

2011. *Fourth break.* Only to be distinguished from No. 2009 by the slightly cleaner bran.

2012. *Chop from fourth break.* Not very different in appearance from 2010, except that it is composed of more finely divided particles.

2013. *Fifth break.* Still cleaner bran than 2011. It still holds a very appreciable portion of endosperm.

2014. *Chop from fifth break.* This chop contains a great deal of branny matter, including pieces of epicarp, endocarp, and embryous membrane. The endosperm is very fine and much mixed with germ. Of course, in all these products, portions of the testa and tegmen are present, but they are not easily seen except in careful preparations.

2015. *Sixth break.* Barely distinguishable from bran.

2016. *Chop from sixth break.* Very largely made up of small pieces of branny material and germs. The endosperm which is present is very fine.

2017. *Bran.* This is composed practically of epicarp, endocarp, and embryous membrane, the cells of the latter having been very little disturbed. There is still a little cuticle and endosperm left, but they have mostly disappeared in previous operations.

2018. *Shorts.* These are made up of all the different parts of the grain in rather a fine condition, some of the branny particles having endosperm still adherent to them.

2019. *Middlings, Uncleaned, No.* 1. These are the largest sized middlings, and consist in themselves of clean, angular fragments of

endosperm, but they are mixed with considerable shorts and many whole and broken germs. They are the most impure of the five, and an analysis will show this fact.

2020. *Middlings, Uncleaned, No.* 2. All the particles are finer than in the previous middlings, and less germ and bran is present, which will produce a corresponding change in their chemical composition.

2021. *Middlings, Uncleaned, No.* 3. Still finer than No. 2, and less bran and germ.

2022. *Middlings, Uncleaned, No.* 4. Finer than No. 3, and less bran and germ.

2023. *Middlings, Uncleaned, No.* 5. The finest of all the middlings, with almost no bran and germ. The effect of cleaning will be small.

2024. *Middlings, Cleaned, No.* 1. Many of the lighter particles of bran removed, but there is much remaining, as well as of the germ.

2025. *Middlings, Cleaned, No.* 2. The bran is to a large degree removed in cleaning these middlings, but the germ, of course, remains.

2026. *Middlings, Cleaned, No.* 3. The bran is almost all gone.

2027. *Middlings, Cleaned, No.* 4. These middlings are practically quite clean and pure endosperm. Only here or there a particle of bran or germ.

2028. *Middlings, Cleaned, No.* 5. Quite clean, and very small in size.

2029. *First middlings, reduction on smooth rolls.* The germ is flattened, and the endosperm reduced in size.

2030. *Chop from first reduction of middlings.* This sample appears to be misplaced, as it contains much bran and germ.

2031. *Second middlings, reduction on smooth rolls.* A sample of this reduction was not furnished.

2032. *Chop from second reduction of middlings.* This chop contains a few particles of bran and germ.

2033. *Third middlings, reduction on smooth rolls.* The germ is prominent in its flattened condition.

2034. *Chop from third reduction of middlings.* The bran and germ have been almost entirely removed.

2035. *Fourth middlings, reduction on smooth rolls.* Like the middlings themselves, merely reduced in size.

2036. *Chop from fourth reduction of middlings.* Here and there a small particle of bran seen.

2037. *Fifth middlings, reduction on smooth rolls.* Resembles of course the fifth middlings.

2038. *Chop from fifth reduction of middlings.* This is not as white as the chop from the fourth reduction, as it contains bran and germ in small quantities.

2039. *Flour from the first reduction.* The grains of endosperm are clean and sharp.

2040. *Flour from the second reduction.* The grains are not as sharp as those from the first reduction.

2041. *Flour from the third reduction.* Very much like the flour from the second reduction, but perhaps a little lumpier.

2042. *Flour from the fourth reduction.* More coherent and yellower than previous flours.

2043. *Flour from the fifth reduction.* There is no specimen of this flour.

2044. *Tailings from middlings purifier, No.* 1. These tailings are coarse. They contain much bran, mixed with germ, and a considerable amount of large middlings.

2045. *Tailings from middlings purifer Nos.* 2, 3, *and* 4. Much finer than the previous tailings and freer from germ and endosperm.

2046. *Tailings from middlings purifier No.* 6. Largely composed of fine endosperm, mixed with bran and germ.

2047. *Tailings from the first reduction.* These are made up of about equal parts of fine endosperm and of bran and germ.

2048. *Tailings from the second reduction.* These are finer than the first tailings, and contain more germ. There are also present pieces of endosperm, flattened like the germ.

2049. *Tailings from the third reduction.* Still finer, with much flattened endosperm, and less grain and bran.

2050. *Tailings from fourth reduction.* Very finely divided and flattened endosperm, with only about 10 per cent. of bran and germ. This should be very evident in the analysis.

2051. *Tailings from fifth reduction.* Coarser than the fourth tailings, and like the third in quality.

2052. *Re-purified middlings.* Coarse pieces of endosperm, with much bran and germ.

2056. *Bakers' flour.* Slightly yellow in color. The grains lack distinctness, making the flour lumpy.

2057. *Patent flour.* A clear, white grain.

2058. *Low grade flour.* The grain is soft and the flour dark and lumpy. Particles of bran and germ are prominent.

2059. *Break flour.* Physically like the bakers' grade in appearance, but particles of bran and germ are present, making it of less value.

2060. *Stone flour.* This flour is white, of a fair grain, with a very little bran.

2062. *Flour from first tailings.* A very good, free grain, but a little branny.

2063. *Flour from third tailings.* A free grain, but quite branny and yellow.

2064. *Flour from second tailings.* This flour resembles that from the first tailings, but contains more bran and is yellower.

2070. *First germ.* This is made up of the finest particles of germ and contains the largest proportion of middlings and bran.

2071. *Second germ.* The largest particles of germ, with little bran and endosperm.

2072. *Third germ.* A medium between the two former.

2074. *Bran-duster flour.* This is black in color and lumpy. It has little grain and a small portion of bran.

2077. *Stone stock, No.* 2. A good middling, with a little bran and germ.

2078. *Stone stock, No.* 3. This is not as good as No. 2, and holds more bran and germ.

2083. *Tailings from sixth break.* This is made up of about half badly shaped and flattened pieces of endosperm, the rest being bran, with a little germ.

2084. *Tailings from first centrifugal reel.* Largely flattened endosperm ; the rest germ, with a little bran.

2085. *Tailings from second centrifugal reel.* These are largely bran and flattened endosperm, with a little germ.

2086. *Tail end of the tailings.* As would be expected, almost entirely bran, with a little adherent endosperm and a small amount of germ. The embryous membrane is still in place ; in fact during the whole process there is very little of it removed from the bran, and were it the chief source of gluten there would be very little in any of the products. This, however, is not the case. It contains little or no gluten, being merely a continuation of the germ, and having a similar composition.

2087. *Dust from No.* 1 *middlings.* This is mostly cuticle epicarp and hairs, with smaller amounts of the more interior parts of the grain.

2088. *Dust from the dust-catcher.* This is all light, fluffy matter, and is made up of small particles from all parts of the grain.

A consideration of the preceding details furnishes us with the following information:

The preparation of the wheat for the rolls removes certain scourings, which consist of cuticle and bran, principally. They are richer in ash and oil than the whole grain and poorer in nitrogen, but, being very small in amount, probably not over one per cent. of the grain, as far as I am able to judge, they produce little effect on the relative composition.

The result of the first break is to show that the floury part of the grain, of which the chop from this break is largely composed, contains less fibre, ash, oil, and albuminoids than the whole wheat. In fact, the interior of the grain of which it is made up is the starchiest part.

So small a portion of the grain is removed in the first break that the feed of the second is about the same in composition as when it entered the first, and as close as the inevitable differences in selecting samples in a large mill will permit. In this break the greater part of the endosperm is separated from the bran.

It is, consequently, the starchiest and has the least ash, oil, fibre and albuminoids of any of the chops.

The feed for the third break, in a corresponding way, shows the effect of the removal of nearly all the endosperm, by largely increased percentages of the same constituents which are deficient in the chop of the previous break. The two analyses show that the bran contains much more nitrogen, ash, oil and fibre than the endosperm, but not, as it appears, necessarily more gluten.

As the wheat continues through the rolls the remaining endosperm is removed, but at the same time more particles of bran and germ get into the chop. The result upon the composition is shown by the rapid increase in the relative percentages of those constituents which have been mentioned as being more prominent in the bran.

The finished bran contains more ash, oil and fibre than any products, but not quite as much albuminoids, owing to the fact that the chop from the sixth break has a large portion of germ and embryous membrane, rich in nitrogen.

Analyses of the Products of Roller Milling.

Serial Number.	Names.	Water.	Ash.	Oil.	Carbhydrates.	Fibre.	Albuminoids.	Nitrogen.	Phosphoric Acid.	Ratio nitrogen to phosphoric acid.	Gluten.	
											Moist.	Dry.
	C. A. Pillsbury & Co., Minneapolis, Minn.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent	Per cent.	Per cent.
2001	Wheat as it enters the mill	9.66	1.91	2.61	69.94	1.70	14.18	2.27	.82	2.77	....	....
2002	Wheat prepared for the rolls	9.07	1.79	2.74	70.37	1.68	14.35	2.30	.82	2.80	32.31	11.88
2003	Cockle and screenings	9.03	2.65	4.32	66.12	4.23	13.65	2.18	.78	2.80	....	....
2004	Scourings removed by cleaners	9.27	3.68	3.73	70.19	1.58	11.55	1.85	.76	2.43	....	....
2005	First break	8.23	1.73	2.68	71.56	1.62	14.18	2.27	.91	2.49	31.92	11.69
2006	Chop from first break	12.52	.88	2.08	70.44	1.13	12.95	2.07	.46	4 50	34.10	12.27
2007	Second break	8.37	2.04	2.47	71.47	1.65	14.00	2.24	.98	2.29	32.78	11.80
2008	Chop from second break	12.78	.57	1.68	71.82	.55	12.60	2.04	.34	5.94	36.88	12.56
2009	Third break	9.92	2.55	5.25	65.10	2.13	15.05	2.41	1.33	1.81	32.09	12.04
2010	Chop from third break	12.70	.78	1.86	71.10	.78	12.78	2.04	.42	4.86	37.19	13.00
2011	Fourth break	8.18	3.30	4.09	66.20	3.00	15.23	2.44	1.44	1.07	27.88	10.54
2012	Chop from fourth break	12.35	1.47	2.87	67 90	1.23	14.18	2.27	.75	5.05	30.52	11.64
2013	Fifth break	7.62	5.16	4.91	61.76	4.80	15.75	2.52	2.58	.98	....	....
2014	Chop from fifth break	11.91	1.99	4.16	64.46	1.73	15.75	2.52	1.01	2.49	27.97	11.82
2015	Sixth break	7.66	5.68	5.34	59.42	5.60	16.28	2.60	2.95	.81	....	....
2016	Chop from sixth break	11.84	3.29	4 92	59.09	3.18	17.68	2.83	1.66	1.70	24.04	10.69
2017	Bran	10.91	5.59	5.03	56.21	5.98	16 28	2.60	2.78	.94	....	....
2018	Shorts	10.94	3.41	4.67	60.28	3 90	16.80	2.69	1.62	1.66	....	....
	Middlings uncleaned —											
2019	No. 1	12.71	1.27	2.73	68.78	1.03	13.48	2.16	.64	3.39	29.68	10.57
2020	No. 2	12 18	1.04	2.16	70.49	.83	13.30	2.13	.54	3.94	32.99	11.49
2021	No. 3	12 27	.70	1.80	71 52	.58	13.13	2.10	.36	5.83	35 52	12.21
2022	No. 4	12.47	.68	1.75	70.69	.58	13 83	2,21	.40	5.52	45.62	15.69
2023	No. 5	12.34	.61	1.75	70.24	.53	14.53	2 32	.33	7.03	43.82	14.86
	Middlings cleaned —											
2024	No. 1	12.67	1.07	2.12	70 16	.85	13.13	2.10	.59	3.56	34.03	11.16
2025	No. 2	9.93	.65	1.90	74.09	.65	12.78	2.04	.33	6.18	....	....
2026	No. 3	12.36	.59	1.70	71.67	.55	13.13	2.10	.24	8.75	44 43	14 99
2027	No. 4	12.51	.52	1.77	71.57	.33	13.30	2.13	.29	7.34	51 93	17.85
2028	No. 5	12.35	.51	1.62	70.74	.43	14.35	2.30	.23	10.00	46.15	14.87
	Middlings, reduction on smooth rolls —											
2029	First middling	12.64	.82	2 56	70.80	.58	12.60	2.02	.46	4.39	34.20	11 57
2030	Chop from first middling	12.74	.72	1.99	71.72	.58	12.25	1.96	.40	4.90	32.16	10.91
2031	Second middling	....	....	....	....	....	....	....	....	....	....	....
2032	Chop from second middling	12.48	.57	1.68	71.24	.38	13.65	2.18	.34	6.41	41.36	13.65

Serial Number.	Names.	Water.	Ash.	Oil.	Carbhydrates.	Fibre.	Albuminoids.	Nitrogen.	Phosphoric Acid.	Ratio nitrogen to phosphoric acid.	Gluten.	
											Moist.	Dry.
		Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
2033	Third middling	12.29	.61	1.86	71.91	.55	12.78	2.04	.34	6.00	36.70	11.81
2034	Chop from third middling	12.73	.79	2.01	71.29	.58	12.60	2.02	.43	4.70	34.58	11.68
2035	Fourth middling	11.43	.56	1.86	73.12	.43	12.60	2.02	.34	5.94	37.00	12.23
2036	Chop from fourth middling	11.72	.50	1.76	72.56	.33	13.13	2.10	.27	7.78	42 06	12.32
2037	Fifth middling	12.21	.65	2.08	71.85	.43	12.78	2.04	.40	5.10	36.25	11.97
2038	Chop from fifth middling	11.47	.56	2.03	72.66	.50	12.78	2.04	.37	5.57	40.84	13.11
	Flour from reduction of middlings—											
2039	First	12.03	.39	1.58	73.70	.25	12.05	1.93	.24	8.04	31.51	10.97
2040	Second	12.42	.44	1.66	72.55	.33	12.60	2.02	.24	8.42	37.04	12.07
2041	Third	11.54	.38	1.36	75 24	.28	11.20	1.79	.19	9.42	32.54	10.99
2042	Fourth	11.58	.40	1.42	72.92	.38	13.30	2.13	.20	10.65	37.90	12.52
2043	Fifth	...	....	....	....	....	....	....	....	....	....	....
	Tailings from middlings purifiers—											
2044	No. 1	12.33	3.30	4.96	60.06	3.25	16.10	2.55	1.61	1.60	....	....
2045	Nos. 2, 3 and 4	11.59	3 09	3.92	....	....	14.53	2.32	1.39	1.67	12.28	7.62
2046	No. 6	12.00	.90	2.37	69.10	1.10	14.53	2.32	.49	4.73	39.88	14 37
	Tailings from reduction—											
2047	First	11.78	3.26	5.03	60.32	2.63	16.98	2.72	1.82	1.47	13.04	5.47
2048	Second	10.35	3.38	4.37	59.87	2.08	19.95	3.19	1.68	1.90	....	....
2049	Third	11.72	2.35	4.37	63.27	1.66	16.63	2.66	1.34	1.98	....	....
2050	Fourth	12.09	.88	4.16	68.47	.40	14.00	2.24	.48	4.67	35.73	13.34
2051	Fifth	12.12	2.29	3.85	63.93	1.18	16.63	2.66	1.35	1.97	1.89	.67
2052	Repurified middlings	11.72	2.11	3.67	65.99	1.63	14.88	2.38	1.21	1.98	28.17	10.74
	Finished Flour—											
2056	Bakers'	12.18	.62	2.00	69.99	.33	14.88	2 38	.31	7.68	51 21	16.97
2057	Patent	11.48	.39	1.45	73.55	.18	12.95	2.07	.18	11 50	36.14	10.85
2058	Low grade	12.01	1.99	3 86	63.26	.93	17.95	2 74	1.16	2.36	10 01	4.26
2059	Break flour	12.48	.58	1.87	69 44	.23	15.40	2.46	.31	7.94	51.38	15.87
2060	Stone flour	12 04	.49	1.61	72.85	.23	12.78	2.04	.27	7.55	38.21	11.74
	Flour from tailings—											
2062	First	12.55	.62	2.93	70 25	.35	13.30	2.13	.30	7.10	39.13	12.85
2063	Third	12.50	.85	2.79	70.20	.53	13.13	2.10	.45	4.67	37.78	12.68
2065	Second	11.20	.76	2.63	72.28	.48	13.65	2.18	.39	5.59	43.25	13.87
2068	Cockle chop	12.45	2.79	4.34	64 01	3.63	12.78	2.04	.86	2.37	....	....
2069	Cockle bran	7.71	3.46	3.84	65.46	9 03	10.50	1.68	.83	2.02	....	....
2070	First germ	8.69	3.42	9.35	53.28	1.23	24.13	3.86	1.83	2.11	....	....
2071	Second germ	8.75	5.45	15.61	35.19	1 75	33.25	5.32	2.57	1.98	....	....
2072	Third germ	7.68	4.94	13 75	39.25	1.50	32.88	5.26	2.56	2.05	....	....
2074	Bran duster flour	11.78	1.17	2.70	70.20	.50	13.65	2.18	.66	3.30	58.59	13.72

Serial Number.	Names.	Water.	Ash.	Oil.	Carbhydrates.	Fiber.	Albuminoids.	Nitrogen.	Phosphoric Acid.	Ratio nitrogen to phosphoric acid.	Gluten.	
											Moist.	Dry.
	Stone stock —	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
2077	No. 2	12.15	.40	1.62	72.91	.25	13.65	2.18	.19	11.58	47.55	15.32
2078	No. 3	12.01	.55	2.12	71.76	.43	13.13	2.10	.28	7.50	46.39	15.15
	Tailings —											
2083	From sixth break	11.64	2.29	4.06	64.31	1.95	15.75	2.52	1.23	2.05	16.45	6.17
2084	From first centrifugal reel	11 42	2.15	3.44	66.56	1.20	15.23	2.44	.98	2.49	6.58	2.39
2085	From second centrifugal reel	11.07	2.85	4.73	61.82	2.20	17 33	2.79	1.47	1.88	....	....
2086	Tail end of the tailings	11.36	3.87	5.23	.....	.....	15.75	2.52	1.75	1.44	10.74	.41
2087	Dust from No. 1 middlings	11.03	1.83	2.73	64.86	5.20	14.35	2.30	.55	4.18	25.78	10.31
2088	Dust from dust catcher	11.53	1.17	2.64	69.01	1.65	14.00	2.24	.55	4.07	35.05	13.00
	HERR & CISSEL, GEORGETOWN, D. C.											
2089	Mixed wheat, clean	9.62	1.93	2.29	71.83	1.55	12.78	2.04	.98	2.08	30.00	11.03
2090	First break	8.13	2.03	2.46	72.30	1.60	13.48	2.16	1.05	2.05	29.17	10.42
2091	Second break	9 47	2.00	2.01	71.81	1.58	13.13	2.10	.91	2.30	34.02	11.87
2092	Third break	8.79	2.03	2.37	71.98	1.70	13.13	2.10	1.10	1.90	29.24	10.32
2093	Fourth break	8.91	2.39	2.33	70.97	1.75	13.65	2.18	1.14	1.91	34.08	12 23
2094	Fifth break	7.18	3.46	....	....	....	15.40	2.46	1 35	1.82	26.75	10.09
2095	Sixth break	9.38	4.76	....	....	....	16.10	2.58	2.46	1.04	....	....
2096	First middling	11.96	.49	1.22	75.30	.35	10.68	1.71	.25	6.84	32.99	9.92
2097	Second middling	11.89	.51	1.21	75.56	.33	10.50	1.68	.25	6.72	35.49	10.55
2098	Third middling	10.88	.50	1.19	75.45	.25	11.73	1.88	.24	7.83	42.10	13.32
2099	First middling through smooth rolls	9.87	1.84	2.00	71.98	1.18	13.13	2.10	.87	2.42	28.97	10.59
2100	Patent flour	12.98	.32	.92	75.60	.20	9.98	1.60	.16	10 00	29.55	9.08
2101	Bakers' flour	13.29	.47	1.26	72.45	1.50	11.03	1.76	.28	6.28	35.04	11.30
2102	Low-grade flour	12.59	1.05	2.33	69.10	.75	14.18	2.27	.58	3.91	35.96	12.81
2103	Germ middlings	11.10	2.41	3.74	66.59	1.63	14.53	2.32	1.19	1.94	....	....
2104	Feed middlings or tailings	8.53	3 75	4.96	62 21	4.10	16.45	2.63	1.98	1.32	....	....
2105	Bran middlings	8.24	6.89	5.52	56.77	6.13	16.45	2.63	.98	2.68	....	....
	WARDER & BARNETT, SPRINGFIELD, OHIO.											
1855	Wheat	9 05	2.06	2.46	71.67	2.33	12.43	1.99	1.03	1.93	20.93	10.34
1856	Patent flour	12 32	.34	1.05	75.28	.33	10.68	1.71	.19	9.00	35.52	10.76
1857	Bakers' flour	11.98	.60	1.77	71.52	1.00	13.13	2.10	.33	6.36	38 29	12.30
1858	Low-grade flour	12 36	.69	1.00	75.04	.93	9.98	1.60	.30	5.33	28.37	9.96
1859	Middlings	8.49	4.28	5.94	60.64	3.15	17.50	2.80	1.12	2.50	....	....
1860	Bran	7.74	6.99	4.99	....	....	15.40	2.46	1.04	2.36	....	....
2190	Patent flour, second sample	13.59	.36	1.08	73.94	.35	10.68	1.71	....	....	....	....

The shorts are poorer in ash than the bran, also in oil and fibre, and this arises, probably, from the origin of the shorts in the more exterior coats of the grain.

The five classes of middlings, graded by sizes, present a regular decrease in ash, oil, and fibre, from the largest to the lowest. The albuminoids do not vary so much in amount, but, as will be seen later, they vary very much in quality. After cleaning, the analyses show what would be expected from the removal of branny particles and germ; but the same general relations are preserved.

The reduction of the middlings, of course, affects their composition but slightly; the tailings, although rich in nitrogen, being small in amount. They, like the tailings from the middlings purifiers, consist largely of bran and germ, mixed with some endosperm, and are therefore, with one exception, in which the tailings are made up of flattened endosperm, rich in ash, oil and albuminoids.

The different grades of flour vary somewhat, but within narrower limits than one would be led to expect from the composition of the middlings. Among the finished flours as graded for market, large differences appear, both in the physical properties and chemical composition. From a cursory glance it might be said that the low grade flour was the best, as it contains the most albuminoids, but its weakness lies in the fact that it has only 4 per cent. of gluten. The bakers' flour contains more ash, oil, fibre and albuminoids, and even more gluten than the patent, but owing to the increased amount of the three first named constituents it is proportionately lacking in whiteness and lightness. The patent flour certainly has the greatest number of desirable qualities.

Several other grades of flour, break flour, stone flour, and flours from the first, second and third tailings, are very similar, and, as far as the analyses go, good. The preliminary examination has, however, shown certain defects in each. The break flour is richer in albuminoids and gluten than any other, and if it were pure and its physical condition good it would be of value.

This process of reducing the middlings to flour is distinguished by the completeness with which the germ is removed by flattening it between rolls and separating it in the bolts. This furnishes three by-products which are known as first, second and third germ. They consist of the germ of the wheat mixed with a certain portion of branny and starchy matter, the second germ being more nearly

pure. They all contain much ash, oil and nitrogeneous substance, and, if left in the flour, blacken it from the oxidation of the oil and render it liable to fermentation, owing to peculiar nitrogeneous bodies which they contain. A proximate analysis appears in my original report.

The flour from the bran-dusters is much like that from the tailings, and like that from the stone stock, from a chemical point of view. This merely shows that chemical evidence alone cannot be depended on; for the bran-duster flour is a dirty, lumpy by-product, while the stone stocks are valuable middlings.

Analyses of the dust from middlings and from the dust-catcher are remarkable, for they both show the presence of much gluten, and of much fibre in the first. This is due to their both containing both bran and endosperm.

To follow the gluten through the different products it is necessary to go back to the breaks. The amount in the various chops does not vary greatly. There is an apparent anomaly in the fifth and sixth breaks, however, where no gluten is found in the feed, but much in the chop. This is owing to the fact that the feed has become so branny at this point that by the usual method of washing to obtain the gluten none is recovered. After it is loosened from the bran in passing through the rolls it is readily collected.

Among the middlings, both cleaned and uncleaned, the fourth is the richest in gluten, and the result of the process of cleaning is to increase the amount, although slightly diminishing the nitrogen, which is due to the removal of the branny matter, which, though rich in nitrogen, is poor in gluten.

In the products of the reductions on smooth rolls the chops from the higher middlings are the richest, and if the analyses of the flours were complete, No. 4 would probably contain more than the lower numbers.

The tailings are remarkable, as has been already said, not so much that No. 1 has no gluten, but that Nos. 2, 3, 4 have 7.62 per cent. and No. 6 as much as 14.37 per cent. The regular increase shows that in the highest numbers it is due to the large portion of endosperm which they were found to contain. No. 1 consists almost entirely of the outer coatings of the grain; Nos. 2, 3, 4, of the same, mixed with a large portion of endosperm, in an attached condition, while in No. 6 it is as difficult to discover anything but

floury material. The small percentage of ash also shows that it can contain but little bran.

In the same way No. 4 tailings, from the reductions, has 13.34 per cent. of gluten, due to the large amount of endosperm which it contains, and in this case, too, the fact is presaged by the low percentage of ash. The remaining tailings of this class have little or no gluten, with the exception of No. 1, as they contain very little endosperm.

The results, as a whole, warrant the conclusion that less gluten is wasted in the by-products than would be imagined. A knowledge of the percentage of each product made is necessary for a complete understanding of this relation.

The analyses of the products of milling Virginia and Ohio wheats by the roller process are not as complete as those of the Minnesota grain. They show variations in the different products, not, however, exactly corresponding ones. Among the flours, for instance, the low grade Virginia, instead of containing less, has more gluten than the bakers' grade. This is probably due to the greater softness of the Eastern wheat, in consequence of which it is less suited to the process. Among the Ohio flours, although the low grade does not exceed the other brands in the amount of gluten which it contains, it approaches closely to them, and it is reasonable to conclude that the hard spring wheats are more suited to the process than the softer winter varieties.

It has been impossible to complete analyses of all the ashes of the differents products which have just been described, but that of the ash of the patent flour shows a marked decrease over that of the original grain in the percentage of magnesia which it contains, made up by a corresponding increase in lime. The phosphoric acid, too, is higher, and determinations of this constituent show that the relation between it and the nitrogen is an intimate one.

Starting with a ratio of 2.8 in the whole grain, with every purification the figure rises until it reaches the highest grade middlings and patent flour; that is to say, as we approach the more perfectly purified products there is a greater loss of phosphates than of nitrogen. The highest ratios are found in the patent flours and the chop and middlings which lead to this product. In the flours from the reduction of different grades of middlings the change in the ratio is gradual, and corresponds

closely to the inverse change in the amount of phosphates in the ash. A high ratio denotes, therefore, a deficiency in phosphates, and this is the chief fault with our high grade flours.

For more complete details in regard to this subject, reference must be made to Bulletin No. 4 of the Bureau of Chemistry, United States Department of Agriculture.

WASHINGTON, *Nov.* 1884.

IV.—THE TIME ELEMENT IN GLUTEN DETERMINATIONS.

BY WM. FREAR.

Few writers on food or plant analysis, in describing Beccari's method for the determination of gluten in grain or flour, make note of the influence of the length of time which elapses between the preparation of the dough and the separation of the starch, upon the quantity of gluten obtained. It has, however, long since been observed by some of the chemists who have given particular attention to the analysis of cereals and albuminoids, that better results are obtained if the dough is allowed to stand for some time before washing: Von Bibra[1] recommends a period of fifteen minutes; Ritthausen[2] makes it thirty minutes; Peligot[3] says that from thirty to fifty minutes is best. Still, though these authors mention definite periods, their disagreement and the fact that in no case are there given experimental data leading to the adoption of the limits named, indicate that they have been arbitrarily selected.

The experiments of Weyl and others having pointed to the conclusion that gluten is produced by the action of an unorganised ferment, MM. Benard and Girardin[4] made some experiments to determine the rapidity and duration of its action. Three equal portions of dough from the same flour were washed, one immediately after preparation, another thirty minutes after, and the third three hours after. The percentages of "moist gluten" obtained from experiments on three samples were as follows:

Immediately.	30 minutes.	3 hours.
24.40	27.40	30.80
26.20	29.20	31.20
22.00	28.20	28.40

[1] Die Getreidearten und das Brod, 1861, p. 140.
[2] Die Eiweisskörper der Getreidearten, Hülsenfrüchte und Oelsamen, 1872, p. 3.
[3] Traité de Chimie Analytique appliquée à l'Agriculture, Paris, 1883, p. 371.
[4] J. Phar. et Chim. (5) **4**, 1881, p. 127–128.

The third sample contained more moisture than the others.

From these results the authors conclude that it is best to wait at least *three hours* before washing.

Recently, in the course of a number of gluten determinations, I was led, without any knowledge of the investigations of MM. Benard and Girardin, to experiment upon the same point. A few trials having shown the great increase during the first thirty minutes, the samples of dough were allowed to stand for longer periods, in order to fix the point at which the formation of gluten was practically complete. In preparing the dough 20 grams of the sample were mixed with 10–15 cc. of water. The results stated in the percentages of "dry gluten" obtained, were as follows:

H. min.	Per cent.	H. min.	Per cent.	Difference.
.45	10.94	2.35	10.76	—.18
.55	11.81	2.35	11.58	—.23
1.00	10.77	3.00	10.75	—.02
1.00	11.01	2.00	11.00	—.01
1.15	11.22	3.40	11.21	—.01
2.15	12.41	3.00	12.77	+.36
1.30	10.55	2.30	9.95	—.60

The last column is surprising because, instead of showing an increase during the longer interval, it seems to indicate an almost invariable decrease. This, however, is explained by the fact that on standing the dough is covered by a pellicle which gradually becomes harder and thicker, and on washing, instead of becoming homogeneous, breaks into small pieces, which will, unless great care be exercised, wash out with the starch, carrying incorporated with them a very considerable portion of the gluten. Thus, No. 7 being an unbolted flour, the loss was much greater because bran renders the pellicle more difficult to soften. In No. 6, the difference in time being small, the increase is more probably due to an accidentally greater loss in the first of the duplicates.

These results, then, indicate that the formation of gluten is practically complete in from forty-five minutes to an hour after the dough is prepared; and that the adoption of a longer period, by increasing the difficulty of the following parts of the process, introduces a source of error rather than a condition favorable to the fairest results.

Contributions from the Chemical Laboratory of Harvard College.

XLV.—ON THE REDUCTION OF CAMPHOR TO BORNEOL.[1]

By C. Loring Jackson.

In 1883, Menke and I published a paper[2] entitled "A New Method of Preparing Borneol from Camphor," in which we described, first, the complete reduction of camphor to borneol by sodium and moist toluol; secondly, a convenient practical method for making borneol by the action of one and a third times the theoretical amount of sodium on an alcoholic solution of camphor, and purifying the product by crystallisation from hot alcohol; and thirdly, explained the formation of the borneol by the following reaction:

$$C_{10}H_{16}O + H_2 = C_{10}H_{18}O.$$

In the first number of the Monatshefte für Chemie[3] for this year, Kachler and Spitzer published an examination of our method, which led them to the conclusion that it was worthless, since in three experiments they obtained products, the larger part of which melted from 179° to 181°, and in no case higher than 185° even after fractional crystallisation and sublimation (borneol melts at 199½°); while another set of experiments showed that as much as 82.8 per cent. of the hydrogen evolved by the sodium in one case, and 54.1 per cent. in another, escaped in the free state. They also determined how much borneol had been formed in one of their experiments by converting the crude product into chlorides, and determining the chlorine, which showed 22.8 per cent. of borneol to 77.2 per cent. of unaltered camphor; and, therefore, doubt whether the formation of borneol was due to reduction by nascent hydrogen at all, but ascribe it rather to the action of the sodium itself, as if in the presence of an indifferent liquid (Baubigny's reaction).

It is to be remarked, however, that they have confined their attention to the reduction of camphor by sodium and alcohol, and were not justified in thus rejecting our reaction,

$$C_{10}H_{16}O + H_2 = C_{10}H_{18}O,$$

[1] From the Proceedings of the American Academy, communicated by the author.

[2] This Journal **5**, 270.

[3] Monatshefte für Chemie **5**, 50.

as they had not repeated the experiment described in the beginning of our paper, in which 25 grams of camphor by the action of an excess of sodium and moist toluol were completely converted into borneol, as shown by the melting-point 197–198°, and a combustion. That this observation, and therefore the reaction given above, are correct, has been proved by Immendorff under the direction of Anschütz, who has published a most welcome paper[1] on the subject in the interval between the appearance of Kachler and Spitzer's paper and this answer, which has been much delayed, because, since the publication of their paper, I have had no laboratory at my disposal until this autumn. Immendorff's proof consisted in increasing the amount of sodium used upon the alcoholic solution of camphor from 1½ to 3½ times the theoretical amount, when he obtained a product which, after crystallisation from petroleum ether or sublimation, melted at 199–200°, and was proved to be pure borneol by analyses of its chloride. Although in this way he confirms our theoretical views, he did not obtain better results from our practical process than Kachler and Spitzer, as he got as low a melting-point (181°) as they, when he used the amount of sodium recommended by us (1½ times the theory), and even with twice the theoretical amount did not get a melting-point above 188°. As we had got a melting-point of 193° for the crude product, I felt that it was advisable to take up the subject again, and study the conditions of the reaction more carefully, especially as both Kachler and Spitzer, and Immendorff, dwell on the interest of this process from a theoretical as well as a practical point of view.

The result of my experiments is, however, that, even when in following our original directions I tried to make the conditions as unfavorable as possible, the melting-point of the crude product was 187–188°, and in other repetitions 188° and 189°, so that my products with one and a third times the theory of sodium melted 6° to 8° higher than the corresponding ones of Immendorff, and as high as his with twice the theory,[2] but not so high as our previous melting-point of 193°. Although, as I could not get such low melting-points as the foreign chemists, I have been unable to find the cause of the difference between their results and ours, I have succeeded in modifying the process for making borneol, so as to make it superior even to the much improved form given to it by Immendorff; for I soon found that a better result was

[1] Ber. d. ch. G. **17**, 1036.

[2] With twice the theory I obtained melting-point 194°.

obtained if less alcohol was used, and upon reducing the quantity by one-half, that is, using five times the weight of the camphor, instead of ten times, as we advised originally, I obtained with one and a third times the theory of sodium a product[1] melting at 193° without purification, while increasing the sodium to twice the theory gave me the same result as Immendorff's with the larger quantity of alcohol, and three and a third times the theory, that is, a crude product having the melting-point 196°, which was not raised by the use of more sodium, and gave by one crystallisation from ligroine[2] 52 per cent., and in a second case 45 per cent. of pure borneol, melting between 199° and 200°. This same melting-point was obtained in four different experiments; and that the yield was not better from Immendorff's method was proved by following his directions carefully in another experiment, the product of which gave, after treatment with ligroine, not more than 50 per cent. of pure borneol. I should judge, too, from the results of my experiments, that cooling and stirring the liquid had a favorable action on the process, but their effect is comparatively small.

The work described above has led me to the following method for the preparation of borneol from camphor, which becomes in this way one of the simplest and easiest operations in organic chemistry: 10 grams of camphor are dissolved in 50 grams of common alcohol in a small beaker, and treated with 6 grams of sodium added in pieces of from 0.1 to 0.2 gram. At first, only two pieces are added at a time, the addition of fresh sodium taking place only after what has been already put in has disappeared; but after the fourth gram, a gram may be added at once, cut in pieces of the size mentioned above. The object should be to keep up a gentle effervescence, and it is well to stir the liquid frequently, to keep it cool by immersing the beaker in a dish of water, and toward the end of the process, when the action has become sluggish, to add from time to time a few drops of water to prevent the liquid from becoming pasty. After all the sodium has been used up the crude borneol is precipitated by water, washed till free from alkali, dried by pressure between cloth or filter-paper, and purified by crystallisation from ligroine.

[1] As this substance is identical with the crude product described in my paper with Menke, I am inclined to think that we must have used less alcohol than the amount recommended by us in that paper.

[2] The crystallisation from ligroine, as recommended by Immendorff, is far superior to the crystallisation from hot alcohol, used by Menke and me.

Finally, I would add that sodium amalgam reduces an alcoholic solution of camphor, although the action is so slow that it is of no value as a practical method, the melting-point being raised only to 183° by action during two weeks, part of the time on the water-bath. The fact, however, deserves mention, because in Beilstein's Handbuch, p. 1763, it is stated that sodium amalgam does not act on camphor.

THE ACTION OF LIGHT ON SILVER CHLORIDE.

By Spencer B. Newbury.

The blackening of silver chloride when exposed to light has been explained in various ways, but the conclusions of even the most careful observers show no agreement, and but little accurate experimental work seems to have been done to clear up the problem. Von Bibra (Journ. f. Prac. Chem., 1875, p. 39) has carefully collected the results of all important observations in this field, and in the same paper gives an outline of his own work on silver chloride and the *subchloride* produced by heating silver citrate in a current of hydrogen and treating the product with hydrochloric acid. The authorities quoted in this paper agree upon the following facts:

1. In the darkening of moist silver chloride by the action of light, chlorine is liberated, apparent by its odor, and easily recognisable by the usual tests.

2. The darkening effect is retarded by the presence of free chlorine, ferric and cupric chlorides, and nitric acid, and accelerated by stannous chloride.

3. Blackened silver chloride is not decomposed by nitric acid; when treated with ammonic hydrate, silver chloride is dissolved, and a residue of metallic silver is left.

In addition, Von Bibra's investigations led him to the following conclusions:

1. Dry silver chloride, exposed to light, with frequent stirring until completely blackened, shows no perceptible loss of weight. The blackened chloride is not decomposed by nitric acid.

2. Silver citrate heated to 100° in a current of dry hydrogen until constant weight is obtained, yields a black powder which is soluble in a very large quantity of cold water, giving a red solution, and which, on treatment with hydrochloric acid, yields pure silver subchloride, the formula of which is Ag_4Cl_3. This compound is decomposed by nitric acid, leaving silver chloride; also by ammonia, leaving metallic silver. Von Bibra concludes that since chloride of silver, blackened by light, is not affected by nitric acid, it cannot be silver subchloride.

As there are on record no accurate observations of a loss of weight on exposing silver chloride to light, I first made this point the subject of a series of experiments. The calculated quantity of silver nitrate necessary to yield .1000 gram of chloride was accurately weighed out, dissolved in 100 cc. of water contained in a flask, and precipitated by the addition of a very minute excess of sodium chloride dissolved in the same quantity of water. The finely divided precipitate remained suspended in the water for a considerable time, subsiding after several hours' exposure to light. The exposed substance was in every case brought upon a weighed Gooch filter (consisting of a platinum crucible, the bottom of which is perforated and covered with a thin layer of asbestos), dried at about 140°, and weighed. By the use of this admirable contrivance it was found possible to reduce to a minimum the experimental errors which have hitherto made observations on this point unsatisfactory.

To ascertain the amount of possible loss, the precipitate produced in the flask was several times directly weighed without exposure to light, with the following results:

	Found.	Calculated.
1.	.0996	.1000
2.	.0997	"
3.	.0997	"

A number of flasks were prepared as described, and exposed for varying periods to direct sunlight; meanwhile a current of air was continuously drawn through the liquid to retard subsidence and carry off liberated chlorine. After the exposure the precipitate was brought on to the filter, dried at 140°, and weighed; then treated on the filter with hot ammonia solution, and finally the filter with the residue of metallic silver dried and weighed again. In every case a distinct loss of weight was observed, and

the residue of metallic silver after treatment with ammonia generally corresponded approximately to the loss of chlorine.

Since the precipitate of silver chloride soon collects at the bottom of the flask as a black, curdy mass, it is evident that but little additional effect will be produced by light after the subsidence is complete.

Four similar flasks, as described above, exposed side by side to direct sunlight for several days, gave the following results:

	Weight.	Loss.	Metallic silver.	Met. silver calculated from loss.
1.	.0967	.0029	.0054	.0085
2.	.0979	.0018	.0076	.0054
3.	.0969	.0027	.0078	.0081
4.	.0982	.0015	.0062	.0045

I am not prepared to offer any explanation of the discrepancies between the amounts of metallic silver found and those calculated from the loss of chlorine. In a very large number of experiments the same lack of agreement showed itself. The figures given serve, however, to prove that there is a distinct and weighable loss of chlorine on exposing silver chloride to light.

Similar experiments were made with the addition of small quantities of stannous chloride. In this case the precipitate is quickly blackened on exposure, soon assuming a gray color, and does not completely subside even after standing some days. On examination the precipitate was found to consist almost wholly of finely divided metallic silver.

In order to ascertain, if possible, whether a *subchloride* results from the action of light on silver chloride, or whether metallic silver only is formed, 10 grams of silver chloride were exposed to the sun under water for several days. During the exposure the substance was frequently stirred to present fresh surfaces to the light, and a current of air was constantly drawn through the liquid, as in former experiments. A small quantity of the resulting dark purple substance, dissolved in ammonic hydrate, left a residue of silver equal to 2.94 per cent. of the amount treated, which gives by calculation a loss of chlorine of .96 per cent. I now hoped to isolate the product of reduction by dissolving out the undecomposed chloride, exactly as in the *fixing* of a photograph. The reagents employed for this purpose were sodium thiosulphate, potassium cyanide, and sodium chloride. In each case, *metallic silver only*

resulted. Even a cold concentrated solution of sodium chloride, frequently renewed, dissolves finally the last trace of silver chloride, and leaves a residue of gray, finely divided metallic silver. The purity of this residue was proved by a number of careful quantitative determinations.

These results certainly lead to the conclusion, that in the blackening of silver chloride by light, metallic silver is formed, and not a subchloride. Otherwise we must assume that the subchloride is decomposed into silver and silver chloride by the action of a cold solution of sodium chloride: which is at least highly improbable. The same conclusion has been reached by other investigators, but the experimental proof given by the action of solvents has been, as far as I know, heretofore lacking. Mr. P. C. Duchochois, whose work is reported in Anthony's Photographic Bulletin for June and November, 1884, concluded that no subchloride is formed, from the fact that after dissolving blackened silver chloride in ammonia, no ammonium chloride is to be found in the solution; supposing the reaction to be as follows:

$$3Ag_2Cl + 4NH_3 = 3Ag_2 + 3NH_4Cl + N.$$

There can, however, be no objection to writing the reaction thus:

$$Ag_2Cl = AgCl + Ag -$$

in which case the ammonium hydrate simply plays the part of a solvent of silver chloride; hence it does not seem to me that the action of ammonia throws any light on the constitution of the substance.

The only remaining evidence of the existence of silver subchloride is the fact that the blackened compound is not dissolved by nitric acid. This fact Von Bibra cites as evidence that the substance is *not* subchloride, since his subchloride prepared from reduced silver citrate *is* decomposed by nitric acid. It has been suggested that the silver may be present in a passive form, but it seems to me more probable that the action of the acid is merely retarded by the presence of a large amount of insoluble chloride. Moreover, I find that long boiling with dilute acid does dissolve some of the silver. A sample of blackened silver chloride which gave on treatment with ammonia 2.94 per cent. silver, showed after boiling three times with fresh additions of dilute nitric acid, 2.74 per cent., 2.26 per cent. and 1.98 per cent. respectively.

I have made many experiments with a view to prepare silver subchloride from the citrate exactly as Von Bibra describes, but although great precautions were taken to thoroughly dry and purify the hydrogen and the silver citrate used, I have never succeeded in obtaining a constant weight. In every case, however, the chloride prepared by acting on the reduced citrate with hydrochloric acid, yielded only metallic silver on treatment with sodium chloride solution. Although I do not regard these last experiments as conclusive, and am at present engaged in repeating and extending them, they are sufficient to strengthen the doubt which many chemists have expressed, as to the existence of the subsalts of silver.

LABORATORY OF CORNELL UNIVERSITY, *Jan.* 10, 1885.

MINERALOGICAL NOTES.

BY EDGAR F. SMITH.

1. PECTOLITE.

This mineral occurs in Lehigh County, Pa., upon limestone and intimately associated with stilbite. Its exact locality is Hosensack Station, on the Perkiomen Railroad. It usually consists of compact masses of acicular crystals, of a grayish color. When reduced to powder the material is woolly and adheres to the pestle. The specific gravity is 2.6. Several analyses were made by Mr. E. B. Knerr and myself, with the following result:

SiO_2	55.17 per cent.
Fe_2O_3	.80
CaO	30.00
K_2O	.37
Na_2O	9.02
H_2O	4.63
	99.99

From what information we have obtained, it would seem that this is the first time that pectolite has been observed in the State.

2. Titanite.

This mineral, rather rare in Pennsylvania, we have also found in Lehigh County, Lower Milford Township, about two miles distant from Hosensack Station. It occurs in the same region in which we observed an olive-colored garnet, previously described in this Journal, Vol. 5, No. 4. The titanite crystals are well defined, but not more than half an inch in length. They are associated with green pyroxene crystals. Their color is a dark brown. Specific gravity 3.45. The analysis of the above made by Mr. Knerr and myself gave:

SiO_2	34.87 per cent.
TiO_2	43.41
CaO	21.75
	100.03

Minerals, from new localities, have been examined in this laboratory as follows:

3. Glauconite, Apophyllite, Heulandite.

By E. B. Knerr and J. Schoenfeld.

The glauconite is from the falls of French Creek, Chester County, Pa., where it occurs in cavities of a feldspar. It has very much the appearance of earthy chlorite. Specific gravity 2.2. The analysis showed:

H_2O	8.43 per cent.
SiO_2	52.86
Al_2O_3	7.08
Fe_2O_3	7.20
FeO	19.48
MgO	2.90
CaO	trace
K_2O	2.23
Na_2O	trace
	100.18

The apophyllite is also found in the same locality. It occurs among the rocks met with in the mining of iron ore. The specimen examined was composed of rather large, well defined forms, having largely developed prism faces. Specific gravity 2.30. The analysis of the above yielded :

H_2O	16.80 per cent.
SiO_2	51.88
CaO	25.31
K_2O	6.30
Fl	...
	100.29

The heulandite is from Adamstown, Lancaster County, Pā. The crystals, although small, show the following faces, ∞P, $(\infty P \infty)$, oP, $-P$, $-2P\infty$, $(2P\infty)$, $(P\infty)$. They are found in cavities and between layers of trap rock. The associated minerals are quartz, calcite, hornblende, and several others, probably zeolites, which could not be examined from lack of sufficient material. Specific gravity 2.2. The analysis showed :

H_2O	16.61 per cent.
SiO_2	57.68
Al_2O_3	17.05
CaO	6.78
MgO	.69
K_2O	1.13
Na_2O	trace
	99.94

4. Menaccanite.

By E. B. Knerr and D. B. Brunner.

This mineral occurs in rather large and good crystals in quartz, near Adamstown, Lancaster County, Pa. Specific gravity 4.6. By analysis we obtained :

	I.	II.	III.
SiO_2	.50 per cent.	.82 per cent.	.90 per cent.
TiO_2	13.31	12.84	13.31
Fe_2O_3	53.36		
FeO	32.38		
	99.55		

5. Stilbite.

By F. P. Davidson.

The specimen analysed was found at Rautenbush, Berks County, Pa. This locality has been already announced,[1] but as no analysis of the mineral is recorded, we give the following:

H_2O	18.46	18.60
SiO_2	58.01	58.15
Al_2O_3	13.75	12.47
CaO	7.76	9.82
MgO	1.38	
K_2O	.42	.43
Na_2O	trace	trace
	99.78	99.47

The usual forms of stilbite were present on the above specimen, the crystals being collected in radiating masses.

6. Stilbite.

By W. S. Hoskinson and D. B. Brunner.

Found at Fegley's Mine, Berks County, Pa., where it occurs upon granite associated with micaceous magnetite. Its usual appearance is in masses of radiating needles of white color. Specific gravity 2.2. Analysed, it shows the following composition:

H_2O	18.97 per cent.
SiO_2	57.54
Al_2O_3	12.67
CaO	7.85
MgO	1.72
K_2O	1.09
Na_2O	trace
	99.84

Wittenberg College, O., *December* 27, 1884.

[1] Genth's Mineralogy of Pa.

REMARKS ON SCHULZE'S PROCESS FOR THE QUANTITATIVE DETERMINATION OF THE HALOGENS IN AROMATIC COMPOUNDS.

By L. P. Kinnicutt and R. C. Sweetser.

K. E. Schulze has recently described a method for determining the amount of chlorine, bromine or iodine in aromatic compounds, where the halogen is united to the carbon atoms of the side chains.[1]

According to this method, an excess of a hot saturated alcoholic solution of argentic nitrate is added to a weighed amount of the compound, the solution boiled for five minutes, and the precipitate collected on a Gooch crucible.

Schulze, for lack of time and material, seems to have tried his method of analysis on only four substances, benzol chloride, benzoyl chloride, and the β-naphthoyl chloride and bromide. Further experiments with the process seemed desirable, and we have on this account analysed a number of the bromine derivatives of phenylpropionic acid, following as closely as possible the method as described by Schulze.

The α-phenylmonobrompropionic acid, $C_6H_5CH_2CHBrCOOH$.

Wt. taken.	Time of boiling.	Br found.	Theory.
0.3191 gram	20 minutes	34.44 per cent.	34.93

The next substance analysed, the phenyldibrompropionic acid, gave only one-half the theoretical amount of bromine; monobromstyrol being formed, which resisted further decomposition.

The phenyldibrompropionic acid ethyl ether, $C_6H_5CHBrCHBrCOOC_2H_5$.

Wt. taken.	Time of boiling.	Br found.	Theory.
0.3087 gram	5 minutes	23.43 per cent.	47.62
0.2860	10	23.74	...
0.2614	20	24.24	...

The α-phenyltribrompropionic acid, $C_6H_5CHBrCBr_2COOH$.

Wt. taken.	Time of boiling.	Br found.	Theory.
0.3191 gram	20 minutes	37.73 per cent.	62.54

[1] Berichte d. deutsch. chem. Gesell. **17**, 1675 American Chem. Journal **6**, 351.

The β-phenyltribrompropionic acid, $C_6H_5CBr_2CHBrCOOH$.

Wt. taken.	Time of boiling.	Br found.	Theory.
0.2950 gram	20 minutes	34.27 per cent.	62.54

The α-monobromcinnamic acid, $C_6H_5CHCBrCOOH$.

Wt. taken.	Time of boiling.
0.2885	20 minutes

No decomposition took place, the solution remaining clear.

The β-monobromcinnamic acid, $C_6H_5CBrCHCOOH$.

Wt. taken.	Time of boiling.
0.3015 gram	20 minutes

No decomposition took place, the solution remaining clear.

The above results seem to prove that although the method described by Schulze can be used in certain cases, its application is a limited one.

CHEM. LABORATORY, WORCESTER INSTITUTE OF INDUSTRIAL SCIENCE.

NOTES ON THE HÜBL METHOD FOR THE EXAMINATION OF OILS AND FATS.

BY RUSSELL W. MOORE.

During the past year the analysis of butter and other fats has received much attention in the chemical laboratory at Princeton. The various methods were subjected to rigid tests, and other fats and oils were also examined by the same methods, in order to ascertain whether they could be used to adulterate butter without fear of detection. The result of this extended examination has been a decided verdict in favor of Reichert's process.

The method of Hehner was found to be liable to pronounce as genuine butter, mixtures of butter with cocoanut oil; while that of Köttstorfer is unreliable from the fact that mixtures of oleomargarine and cocoanut oil were made in such a manner as to come within the prescribed limits.[1]

Recently the method of Hübl,[2] based on the amount of iodine

[1] Chemical News, December 5th, 1884.

[2] Dingler's Polytechnisches Journal 253-281, and abstracted in American Chemical Journal, November, 1884.

absorbed by oils and fats, has been examined. All oils and fats consist of various proportions of the glycerides of the fatty acids of the acetic, acrylic and tetrolic series. These glycerides are acted upon differently by iodine according to the series to which they belong; the acetic series remaining indifferent, while each molecule of the acrylic unites with two atoms of iodine, and each molecule of the tetrolic series with four.

Although the acids behave thus differently towards iodine, the amount of this element absorbed by any given oil is constant. Thus by treating any oil or fat with an excess of iodine, and, after the lapse of some time, estimating the excess by a standard solution of hyposulphite of sodium, the amount of iodine absorbed can be obtained.

By this process Hübl has examined a large number of oils and fats, and has obtained results varying, from Japanese wax, which absorbs but 4.5 grams of iodine per 100 grams, to linseed oil, which will absorb as high as 160 grams.

The following results were obtained in strict accordance with the directions laid down by the author in the original article. The process was found to be most convenient and expeditious, and the transition point of the final titration is extremely sharp. The author recommends the following amounts to be taken for analysis:

Drying oils,	.2	to .3	gram.
Non-drying oils,	.3	.4	"
Solid fats,	.8	1.0	"

My experience has been that it is best to take the lowest amounts recommended, as an excess of iodine is thus secured.

The following results were obtained by duplicate analyses, and the "iodine figures" or amounts of iodine absorbed by 100 grams of oil for the most part agree closely with those given by Hübl:

Linseed oil,	155.2
Poppy oil,	134.0
Cottonseed oil,	108.7
Rapeseed oil,	103.6
Benne oil,	102.7
Sweet almond oil,	98.1
Mustardseed oil,	96.0
Peanut oil,	87.4
Olive oil,	83.0
Lard (melted in laboratory),	61.9

Palm oil,	50.3
Oleomargarine No. 2,	50.0
" No. 3,	50.0
Butter I,	32.8
" II,	19.5
" III,	38.0
Cocoanut oil,	8.9

The process, while furnishing an excellent means for detecting mixtures of some oils, as, for example, olive oil with cottonseed or benne oils, is of no practical value for the examination of butter for foreign fats; since oleomargarine and lard, the ordinary substitutes for butter, have iodine figures considerably higher than that of butter, while that of cocoanut oil lies much below. Thus a mixture might be made of lard and cocoanut oil or oleomargarine and cocoanut oil which would have the same iodine figure as butter. In proof of this the following mixtures were made and examined:

I. { Lard, 40 per cent. / Cocoanut oil, 60 } Iodine figure 32.2

II. { Oleomargarine, 55 per cent. / Cocoanut oil, 45 } Iodine figure 35.5

III. { Butter I, 50 per cent. / Oleomargarine, 27.5 / Cocoanut oil, 22.5 } Iodine figure 35.4

The specific gravity of the cocoanut oil used was .9167 at 37.7° C., which is sufficiently high to bring the mixtures above the specific gravity of .911, which is taken to be that of butter.

The amount of iodine absorbed by different butters varies widely. In eight samples Hübl found a maximum figure of 35.1, and a minimum of 26.8. He also observes that when the fat has undergone any serious decomposition the iodine figures will fall much lower. The truth of this remark is seen in Butter II, which was in a very advanced stage of decomposition, and gave figures considerably lower than the lowest obtained by Hübl.

A comparative view of the results of the examination of several samples by the four different methods is here given:

	Hehner.	Köttstorfer.	Hübl.	Reichert.
*Oleomargarine 2,	95.56	197.4	50.0	.6
* " 3,	...	195.0	50.0	.4
*Butter II,	86.01	227.0	19.5	13.25
* " III,	86.49	224.0	38.0	13.1
Mixture III,	89.50	227.5	35.4	8.7

The samples starred were examined by the Hehner, Reichert and Köttstorfer methods by Professor Cornwall, and the results embodied by him in his report to the New Jersey State Board of Health for 1884.

Butter II was examined by these three processes while fresh, but not by the Hübl process until it had undergone serious decomposition.

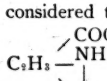
Thus cocoanut oil, as in the case of the Hehner aud Köttstorfer methods, would also rob that of Hübl of any practical value in the examination of butters, while the claim of the Reichert process to be the only one to give reliable results remains unimpaired.

JOHN C. GREEN SCHOOL OF SCIENCE,
PRINCETON, N. J., *January* 24, 1885.

ON THE ACTION OF METHYL IODIDE ON ASPARAGINE.

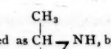
BY ARTHUR MICHAEL AND JOHN F. WING.

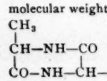
In 1879 P. Griess[1] investigated the action of methyl iodide on asparagine, and obtained, beside tetramethylammonium iodide, a new acid, formed from asparagine by the elimination of a molecule of water. This acid was shown to be monobasic, and was considered the lactimide[2] of aspartic acid, with the constitution



. The formation of such a compound by the action of methyl iodide on asparagine, seemed to us to be open

[1] Berichte, 1879, 2116.

[2] Lactimide is generally considered as  , but there is hardly any doubt that its molecular weight is double that of the above compound, and its constitution is represented by



to considerable doubt, and we made the following experiments in the hope of better establishing its constitution.

We can confirm Griess' statement on the preparation of the acid, and have nothing to add to his description of it except that it melts, under decomposition, at 217°. An analysis of the acid melting at that temperature gave the following results:

	Theory for $C_4H_5NO_3$.	Found.
C	41.74	41.76
H	4.35	4.81
N	12.17	11.75

If the constitution proposed by Griess be correct the acid should be reconverted into aspartic acid by treating with strong mineral acids. The substance dissolved in concentrated hydrochloric acid on heating, and, on boiling the solution, a separation of a crystalline substance was noticed. A further amount of the same substance was deposited from the solution on cooling. This compound was purified by crystallisation from water, and was shown to be fumaric acid, by its properties and by the following analysis:

	Theory for $C_2H_2(COOH)_2$.	Found.
C	41.39	41.66
H	3.44	3.72

It is not necessary to use strong acid to convert the so-called asparaginimide into fumaric acid, as boiling it with dilute hydrochloric acid causes the same decomposition, although it is somewhat slower in its action. This decomposition is also effected by heating with alkalis. Boiled for several hours with caustic soda an evolution of ammonia was noticed, and a precipitate of fumaric acid was formed on addition of an acid. The formation of fumaric acid by the action of acids and alkalis shows quite conclusively that the constitution proposed by Griess cannot be correct, for such a substance should give aspartic acid, which we have shown to be stable toward acids at a much higher temperature than employed in the reaction.[1] The following experiment gives further evidence as to the improbability of the constitution suggested by Griess. Aspartic acid was dissolved in caustic potash and methyl alcohol and a weight of methyl iodide added equal to that of the substance taken. The solution was kept alkaline, and methyl

[1] Berichte, 1885, 2984.

iodide added until no further reaction took place. About five times as much methyl iodide was needed as aspartic acid. The solution was heated until the methyl alcohol was expelled, and gave, on addition of an acid, a deposit of fumaric acid.[1] It is evident that if the substance were asparaginimide, that substance should also have been found in this reaction.

The properties of the substance agree perfectly with those of the acid amide of fumaric acid, and the action of methyl iodide on asparagine may be represented as follows:

$$C_2H_3NH_2\begin{matrix}CONH_2\\COOH\end{matrix} + 4CH_3J = \begin{matrix}CH{-}CONH_2\\|\\CH{-}COOH\end{matrix} + (CH_3)_4NJ + 3HJ.$$

It still remained an open question whether the compound is not the acid amide of maleic acid, since that acid goes over into fumaric acid on boiling with hydrochloric acid. For the purpose of proving this point, the following experiment was made: Two grams of the amide were dissolved in glacial acetic acid, and an equivalent amount, in proportion of equal molecules, of bromine added. The solution was allowed to stand several days at ordinary temperature, when the bromine had disappeared in greater part and a crystalline substance was deposited. The deposit proved to be unchanged acid fumaramide. The filtrate evaporated on a water-bath left a residue, and was purified by several crystallisations from hot water.

A bromine estimation gave the following result:

0.2546 gram of substance gave 0.3486 gram of AgBr.

	Theory for $C_2H_2Br_2\begin{matrix}CONH_2\\COOH\end{matrix}$.	Found.
Br	58.18	58.26

The dibrom-compound crystallises from water in colorless, rectangular plates that decompose without melting. If the original compound is the acid amide of fumaric acid, the β-dibromsuccinic acid should be obtained by treating it with strong acids, whereas if it is a derivative of maleic acid it should yield the α-dibrom acid. On heating the amide with strong hydrochloric acid it dissolved, and, after heating a short time, deposited small white crystals on cooling. These crystals were purified by crystal-

[1] It seemed possible that this fumaric acid should show optically active properties, as it was formed from aspartic acid at a low temperature. It is, however, without action on polarised light, as is also the acid fumaramide.

lisation and corresponded in their properties; they decomposed on heating to 205° to β-dibromsuccinic acid. This experiment shows that the product of the action of methyl iodide on asparagine is the acid amide of fumaric acid.

The close analogy shown by ethyl iodide in its reactions to those of methyl iodide would have led to the supposition that the acid fumaramide would also be formed in its action on asparagine, but several experiments show that this is not the case. Under the same conditions that methyl iodide acts on asparagine, an alcoholic, alkaline solution of ethyl iodide is entirely without action either on asparagine or aspartic acid. A reaction takes place when an alcoholic, alkaline solution of aspartic acid and ethyl iodide is heated to 100° in a sealed tube, but fumaric acid is not formed in the reaction.

The splitting off of ammonia from aspartic acid by the action of methyl iodide is certainly an unexpected reaction, since that acid is stable under conditions which seem much more favorable for such a decomposition. It is possible, however, that if dimethyl-aspartic acid could be obtained it would be found that it has a less stability, and the elimination of ammonia from aspartic acid is due to the previous formation of the dimethyl derivative; which, under the action of a strong alkali and methyl iodide, is decomposed into dimethylamine and acid .fumaramide; the base is then converted into tetramethylammonium iodide by the further action of methyl iodide. It would be of interest to investigate the action of methyl iodide in other amido-acids, such as glutamic acid and tyrosine.

TUFTS COLLEGE, MASS., *Feb.* 1885.

REVIEWS AND REPORTS.

A TREATISE ON THE PRINCIPLES OF CHEMISTRY. By M. M. Pattison Muir, M. A., F. R. S. E., Fellow and Prælector in Chemistry of Gonville and Caius College, Cambridge. Cambridge: at the University Press, 1884.

When one sits down and calmly thinks over the present state of chemistry as illustrated by the way in which most chemists regard the problems of their science, the conviction is easily reached that the methods of investigation now in vogue are far from ideal. The great problem to be solved is, of course, the nature of chemical action. What are the distinctive features of the simplest chemical reaction? What, for example, can we learn in regard to the action of hydrogen upon chlorine? As is well known, the almost universal tendency is to consider the nature of the substances brought together, then to shut the eyes, and, after the action is over, see what has come of it. An enormous amount of valuable information, and, indeed, most of the knowledge of chemical action we possess, has been gathered in this way. And for obvious reasons: the interval between the bringing together of the substances and the formation of new ones is generally so brief that no method of observation will reach it. Though this is not always true, it must be acknowledged that the difficulties in the way of making accurate observations at different stages during the accomplishment of chemical reactions are very great. Hence, most chemists have preferred, and now prefer, to occupy themselves with problems concerning the composition of substances, and it is highly probable that for many years to come most of the work done will be in the same direction. Fortunately, however, there always have been, and there are still, those whose thoughts tend toward that important interval of action which we ordinarily ignore, and slowly facts are discovered which throw light upon it. These facts are described in different journals, and generally without reference to each other, so that it is a difficult matter, for one who does not devote a large amount of time to the task, to coördinate them and see exactly what bearing they have upon the fundamental problems of chemistry.

In the book which forms the subject of this notice the author gives the results of his studies in the field referred to, and also treats of other matters which are of fundamental importance to chemistry regarded as a science. To quote from the preface:

"It (the book) is addressed to students who have already a considerable acquaintance with descriptive chemistry, but it is hoped that by such students the book will be found complete in itself; so that while it certainly deals with chemical principles and

theories on the supposition that its readers have some knowledge of chemical facts, yet the book may fairly claim to rank as a systematic treatise on chemical philosophy. . . . .

"The book is divided into two parts. The first part is occupied with the statement and discussion of the atomic and molecular theory, and the applications thereof to such subjects as allotropy, isomerism, and the classification of elements and compounds. Somewhat full accounts are also given, in this part, of thermal, optical, and other departments of physical chemistry, in so far as the results and methods of these branches of the science are applicable to the questions regarding the composition of chemical systems which are connoted by the term Chemical Statics.

"The second part of the book is devoted to the subject of dissociation, chemical change and equilibrium, chemical affinity, and the relations between chemical action and the distribution of the energy of the changing system. These, and cognate questions, I have ventured to summarise in the expression, Chemical Kinetics."

In regard to the first chapter which treats of atoms and molecules, it need only be said that the subject is looked at in much the same way as the majority of chemists look at it at the present day. Instead, however, of stating dogmatically that bodies consist of molecules, and molecules of atoms, the author brings forward the facts, and shows how the prevalent views have been evolved by a consideration of the facts. In regard to the molecular theory he says: "No theory asserting the continuity of matter has been found capable of explaining the observed phenomena of matter; hence, to accept the molecular theory is, at present, the only feasible working hypothesis, is simply to obey the dictates of the scientific method."

Having reached the conclusion that matter consists of molecules, the next step is to investigate these molecules, and to see what evidence can be gained concerning their complexity. The author regards the study of the phenomena included under the head of nascent actions as of importance in this investigation, and hence considers with some degree of fulness the work of Brodie, Gladstone and Tribe, Tommasi and Traube. The work of Traube on the conditions under which hydrogen peroxide is formed, is taken up in detail. The result reached is, that the hypothesis according to which in nascent action we have to deal with the action of atoms furnishes a satisfactory, partial explanation of the phenomena, but that other things must be taken into consideration. In the action of nascent hydrogen, for example, the effects are due, not only to the hydrogen, but also to the other substances present. "Hydrogen, as it is produced by the action of sodium-amalgam, appears to possess properties different from those which characterise hydrogen produced by the action of zinc on dilute sulphuric acid; attempts to explain these apparent differences lead to fresh researches; we become impressed with the conviction that chemistry is not the study of this element or that, regarded as a kind of matter with certain fixed physical proper-

ties, but that processes of change are the subject-matter of the science, and that to explain any one of these we must take into account each and all of the reacting bodies, and each and all of the conditions under which the total change is proceeding."

Next the *dualistic theory* of molecules as introduced into chemistry by Berzelius, and the *unitary theory*, or *theory of types*, which took its place, are considered, and the subject of *equivalency of atoms* is then taken up. The author is largely influenced by Lossen's views in his treatment of this subject. He closely follows Lossen's method in dissecting the prevalent notions in regard to valency, bonds, saturated and unsaturated compounds, and like many others is strongly impressed by the imperfections of these views. He does not, however, for this reason propose to abandon them entirely, but rather he attempts to find out what is of real value in them and to emphasise this. He holds that "from a consideration of solid or liquid compounds only no trustworthy conclusions as to the valencies of the atoms in the molecules of these compounds can be deduced"; and "that it is certainly better—in the present state of knowledge—to apply the theory of valency only to gaseous molecules."

Passing on we find next a section devoted to the subjects of *Allotropy* and *Isomerism*. Inquiring into the causes of the many facts included under these heads the author says: "Granting that variations in the properties (chemical and physical) of molecules accompany variations in the atomic configurations of these molecules, it is conceivable that the latter variations may consist of

"(1) Variations in the relative positions of the atoms.

"(2) Variations in the distances between the atoms, their relative positions being constant."

Among the arguments brought forward against the latter conception is this: "If the second of the two suppositions is correct, then any molecule containing two atoms should be capable of existing in more than one modification; in other words, every diatomic molecule should be capable of showing isomerism. But there is no certainly established instance of isomerism exhibited by any molecule containing less than three atoms; therefore, as the assumption that variations of properties exhibited by compounds having the same composition and same molecular weight are connected with variations in the relative positions of the atoms composing the molecules of these compounds, suffices to explain the vast majority of well-authenticated cases of isomerism among gaseous molecules, we conclude that it is better, at any rate at present, to build the general theory of isomerism on this hypothesis."

The treatment of the connection between the chemical facts and the prevalent views regarding the constitution of compounds is hardly full enough for the purposes of the book; and so many objections are raised to chemical methods of determining constitution that a student who is not far advanced, and who does not

thoroughly understand the methods, would be led to underestimate their value. The author so delights in the unusual that he is apt to magnify what he calls "residual phenomena." It is plain, however, that on the whole he is in accord with the majority of chemists in regard to the subject of constitution, while he justly censures that too prevalent method of dealing with the problem which results in "those ingenious pictorial representations which are sometimes called the structural formulæ of mineral compounds."

Chapter IV is devoted to the "*Application of physical methods to questions of chemical statics.*" Of the physical methods the first considered are the thermal methods. The subject is treated clearly; indeed it would be difficult to find anywhere a more satisfactory statement in regard to the methods and results of thermo-chemistry than we here have included within fifty-odd pages. After showing that the thermal value of even the simplest chemical change is really the sum of various changes, some of which have a positive and others a negative value, and that in most, if not all cases, it is impossible to assign values to each of the simple changes involved, the conclusion is drawn, that until "the distinction," implied in the terms atom and molecule, "is practically recognised in thermal chemistry, we cannot expect any great advances to be made in applying the mass of data already accumulated to questions of chemical actions and reactions."

Regarding the *law of maximum work* the statement is made that it "is simply a crude application of the principle of the degradation of energy; the principle, namely, that energy always tends to run down from a more available to a less available form. Inasmuch as the production of a chemical compound, with evolution of heat, is an instance of such running down of energy, from the form of chemical affinity to that of heat, it follows that the reversal of this process will require expenditure of work. But the *law of maximum work* does not attempt to analyse the expression *chemical affinity*. Under this head Berthelot includes actions and reactions of different kinds. This is at once apparent from the statement in the *Essai*, that the first fundamental principle of thermal chemistry, viz. "The quantity of heat evolved in a reaction measures the sum of the physical and chemical changes which occur in that reaction"—furnishes the measure of chemical affinities.

"Berthelot's work is saturated with the conceptions of the molecular theory; but, by some fatal perverseness, he refuses to apply this theory to chemical phenomena. While recognising the existence of molecules, and building his generalisations on a molecular foundation, he refuses to accept the conception of atom, or rather he hopelessly confuses it with that of equivalent. The molecule is for him a definite and definable portion of matter, the parts of the molecule are only numbers."

This criticism may sound harsh, but it appears to be just. At

all events we shall be glad to hear what the disciples of Berthelot may have to say in reply. We commend this part of the book to the careful attention of those who have blindly "pinned their faith" to investigations in the field of thermo-chemistry. While something has been learned and much more will be learned in regard to the nature of chemical action by a study of thermal phenomena, it must be acknowledged that the results thus far reached are extremely meagre.

Under the head of *Optical Methods*, the well-known investigations of Gladstone and Dale, Landolt, and Brühl, on the specific rotatory powers of chemical compounds, are fully considered. In regard to van't Hoff's hypothesis which assumes the presence of an *asymmetric carbon atom* in every substance which exhibits rotatory power, and supposes the four bonds of this carbon atom to act in definite directions, the author remarks: "We may object to the extremely crystallographic character of the van't Hoff hypothesis, and to the length to which it pushes the vague notion of 'bonds' or 'units of affinity,' for it seems to regard these as capable of definite arrangement in space; but I think the hypothesis is worthy of careful consideration, because it draws attention to the inadequacy of the prevalent conceptions regarding isomerism and molecular structure, and because it bases the explanation it has to give of the connection between such structure and the properties of compounds on essentially dynamical conceptions."

In Book II which treats of CHEMICAL KINETICS the student will find much that has not been considered in other treatises in the English language. The first chapter is devoted to *Dissociation*, the theories of Pfaundler and Horstmann being specially considered. The subject of the second chapter is *Chemical Change*. After a brief reference to the views of Berthollet, Davy and Berzelius on this subject, the author says: "These great chemists were agreed in regarding the object of chemistry to be an explanation of the changes which matter undergoes; they did not think that the ability to give an account of the physical properties of each kind of matter sufficed to make one a chemist. Chemical change was, for them, continuously proceeding, but it might be checked by the action of electrical, or thermal, or other forces. Their fundamental conception is clearly that of an equilibrium resulting from the actions of different forces, the principal of which are chemical, electrical and thermal." The object of the chapter is "to gain a general view of the conditions and the course of chemical actions." The "facts which must some day find their place in a general theory of chemical action . . . . may be roughly classified under four heads: (1) contact-actions; (2) predisposing affinity; (3) induction; (4) influence of mass."

Recent researches, more particularly those of Guldberg and Waage, have thrown considerable light on facts included under the fourth head.

The studies on the influence of mass lead to the conception of

chemical equilibrium, "of every chemically stable system as being in a condition of equilibrium, which is the result of the actions of various forces, some of which are what we usually call chemical, and others physical." Pfaundler's hypothesis of chemical equilibrium is considered, and we are then told that though considerable space has been devoted to it, "it is questionable whether hypotheses such as this are of much scientific value. We have no exact knowledge of the forces acting between the parts of molecules; and we know almost nothing of the mechanism whereby the energy absorbed by this or that substance is employed." Then a paragraph is devoted to Horstmann's "thermodynamical theory of dissociation, which is also applicable, in its broad features, to other cases of chemical equilibrium." "But," says the author, "the whole subject of chemical equilibrium has been treated in a masterly manner by Willard Gibbs." A good account of Gibbs' well-known papers which appeared in the *American Journal of Science and Arts* then follows, and the great importance of these papers is pointed out.

One of the most interesting chapters in the book is that in which the subject of *Affinity* is considered. After a reference to the first views concerning affinity it is stated that "when we come to more recent times, it is very difficult to gain a clear conception of the meaning of the term affinity." "Measurements of the quantities of heat evolved or absorbed during definite chemical changes appear to afford the easiest means of measuring gains or losses of energy, and in this way of the comparative magnitudes of the affinities of different substances.

"But before we can hope to gain exact measurements of affinity, we must have a clear conception of what it is we want to measure. Affinity, I think, is usually regarded as an action, or sometimes as the cause of an action, of some kind, which occurs between the atoms of chemical elements, such action resulting in a loss, or gain, of energy to the system of which these atoms are the constituents. Now, it is possible that chemical affinity may be analogous to electrical potential; that as the existence of a difference of electrical potential between two particles implies the possibility of electrical work being done, so the existence of what might perhaps be called chemical potential between two atoms, means the possibility of chemical work being done. If this supposition were adopted, we should look to electrical methods for the means of investigating chemical affinity.

"To sum up, we may regard affinity as essentially connected with interatomic, and perhaps intermolecular, actions; and we may attempt to obtain measurements of different affinities by electrical methods; or we may be content to connect the term affinity with the actions and reactions which occur when two, or more, chemically distinct substances combine to form new substances; and we may seek to deduce measurements of these actions, either from the velocities of the chemical changes, or from

the conditions of equilibrium of the changing systems, or from observations of the changes of the energies of the reacting bodies.

"The more important attempts which have been made to solve the problems of affinity may all, I think, be classed under these headings. Most important work has been done by Guldberg and Waage, and by Ostwald, in framing and applying a theory of affinity founded on measurements of the velocities of chemical changes, and of the conditions under which equilibrium is attained by given systems.

"Berthelot and Thomsen have devoted themselves chiefly to the thermal aspects of the subjects. Helmholtz, following on the older work of Berzelius, Faraday, Joule and Thomson, has recently made some advances in applying electrical methods to these questions."

After reviewing the works of the authors mentioned, it is shown that the nearest approach to measures of affinity is reached in the results of Ostwald, who has determined what he calls "affinity constants." "These affinity constants are true equivalents; they express power of doing definite amounts of chemical work." It is then further pointed out that, though chemical affinity cannot as yet be satisfactorily measured by thermal methods, these methods may, nevertheless, throw light on the differences between the affinities of substances in various analogous reactions. Speaking of the possible applications of electrical methods for determining affinities, the author quotes the remark of Helmholtz, who says: "I think the facts leave no doubt that the very mightiest among the chemical forces are of electrical origin. The atoms cling to their electric charges, and opposite electric charges cling to each other, but I do not suppose that other molecular forces are excluded, working directly from atom to atom." Until we attach a more definite meaning to it than we do at present the author questions whether it is desirable to retain the word affinity.

From the above sketch some idea of the character of Mr. Muir's book may be gained. For the earnest student, however, this should not suffice. The study of the book can only tend to clearer thinking than is common among students of chemistry, and to thinking on subjects which are of fundamental importance, though usually ignored. There can be no question of the fact that the thoughts of leading chemists are tending towards the subjects treated of under the head of Chemical Kinetics, and we may confidently look for the rapid and important developments of these subjects. Those who have made up their minds that the study of constitution is the one thing needful will find before many years that discussions are taking place which they cannot comprehend. Those who have reached or passed middle life may, perhaps, not become painfully aware of their ignorance before they pass away, but surely it is the duty of younger men who have just entered upon their career and who have high ideals, to familiarise themselves with the subjects which are considered in Mr. Muir's book.

The treatment will be found clear and logical, and the book can be cordially recommended to those who will take the trouble to think, and will not condemn simply because the views of an author may not happen to coincide with those to which they are accustomed. It must be said that Mr. Muir is nothing, if not critical, but it cannot be claimed that he indulges to any great extent in hypercriticism. His remarks which seem most severe are evidently prompted by the desire to find the truth, and having found it, he holds it up stripped of the dross with which it is too frequently covered.

I. R.

NOTE IN REGARD TO THE INFLUENCE OF MAGNETISM ON CHEMICAL ACTION.

Some time ago[1] I described an experiment which seemed to prove that chemical action is, under some circumstances, influenced by magnetism. I afterwards found that somewhat similar experiments had been performed by Robert Hunt,[2] and that after Hunt, Wartmann[3] had worked on the subject, and had come to the conclusion that magnetism does not influence chemical action. In 1882, at the Fall meeting of the National Academy of Sciences, I gave an account of later experiments by myself, and stated that the work would be continued. In 1883, in Vol. I, No. 2, of "Science," I published a short paper, in which I called attention to the fact that I was engaged in repeating Hunt's experiments, and I proposed to continue the investigation as long as there seemed promise of obtaining results of value. The work has suffered some interruption since then, but has at no time been given up. The unsatisfactory results reached in repeating Hunt's experiments have interfered with work in new and more profitable directions. Lately I have secured the services of an assistant, and am now pushing the investigation forward as rapidly as the character of the work will permit. We have already obtained some extremely interesting results in depositing various metals upon iron and nickel under the influence of a powerful magnet, and we are now engaged in the study of the action of various acids on metals. We have found that when iron in a magnetic field is treated with nitric acid, certain parts of the iron are protected, while other parts are dissolved with varying degrees of rapidity according to the position with reference to the protected parts. Experiments with hydrochloric acid give similar results, though it appears that the parts protected are not the same as in the case of nitric acid. A full account of the results reached will be published in due time. The object of this notice is merely to call the attention of other workers to the fact that my work on the general subject of "Chemical Action in a Magnetic Field" has not been abandoned, and that through the aid of the Trustees of the Bache Fund

[1] This Journal, **3**, 157. [2] Philosophical Magazine [3], **28**, 1. [3] *Ibid.* [3], **30**.

it is now in my power to continue it without interruption. I have no desire nor right to prevent others from working in the same field, but I should be glad to communicate with any one who may contemplate undertaking such work, as unnecessary duplicating may thus be avoided.

IRA REMSEN.

To the Editor AMERICAN CHEMICAL JOURNAL:

Sir:—I notice in No. 4, Vol. 6, an article by A. H. Elliott, on Water Gas Tar. An examination of this tar was commenced about a year since by Mr. G. P. Adamson, of this laboratory, and is now nearing completion. He finds that the tar contains an unusually large amount of water, that it is very rich in naphthalene and anthracene, and is free from phenols and amido compounds. The light oil dissolves completely in sulphuric acid, showing that it is free from paraffins. This tar forms an excellent source of pure naphthalene, as this can easily be obtained perfectly pure. Further results will be offered in due time.

EDWARD HART.

LAFAYETTE COLLEGE, *Nov.* 1884.

OBITUARY NOTES.

HANS HÜBNER, the head of the Chemical Laboratory at Göttingen, died suddenly July 13, 1884. Hübner was born in 1837, in Dresden, and became connected with the University of Göttingen as associate professor in 1870. He was made full professor in 1874, and, after Wöhler's death, he directed the entire work of the laboratory. He contributed very largely to our knowledge of isomerism phenomena in the aromatic series. He was an excellent teacher, and was highly respected by his students.

HERMANN KOLBE, Professor of Chemistry in the University of Leipsic, died November 25, 1884. He was born in the year 1818, at Elliehausen, near Göttingen. He studied under Wöhler from 1838 to 1842. From 1842 to 1845 he was an assistant of Bunsen, and in 1846 assistant of Lyon Playfair, in London. In 1851 he became professor of Chemistry at Marburg, succeeding Bunsen in this position. Finally, in 1865, he was called to Leipsic to succeed O. B. Kühn. Kolbe has always been an industrious worker, and achieved results of the highest importance. He and Frankland were certainly the first to call attention to the fact that the carbon atom can unite with only a certain fixed number of other atoms, and this prepared the way for the introduction of the conception of valence. Kolbe first pointed out that organic acids are to be regarded as analogous to formic acid, containing radicals in the place of the

hydrogen of this acid; and that the organic acids bear the same relation to carbonic acid that the sulphonic acids bear to sulphuric acid. With the aid of a keen insight into the nature of alcohols, he was enabled to prophesy the discovery of secondary alcohols and to describe their general properties before they were discovered. As evidence of the literary activity of Kolbe may be mentioned the following works: Ausführliches Lehrbuch der organischen Chemie, in 3 large volumes; Kurzes Lehrbuch der anorganischen Chemie, 1877, 2. Auflage, 1884; Kurzes Lehrbuch der organischen Chemie, 1883. For many years past Kolbe has bitterly opposed the methods of modern chemistry. A careful study of his papers will show that the particular feature of modern chemistry which aroused his ire is the tendency to speculate upon an insufficient basis of facts. He did not object to structural formulas, as such, for he himself used them constantly, but he did object to the free use of these formulas by those who do not comprehend them, and to whom they convey no idea regarding the chemical conduct of the substances represented. In some fundamental matters Kolbe differed from the majority of chemists. His ideas regarding the hydrocarbons, for example, were based upon the conception that the four hydrogen atoms of marsh gas are not equivalent.

HENRY WATTS, F. R. S., Editor of Watts's *Dictionary of Chemistry* and of *The Journal of the Chemical Society* of London, died June 30th, 1884. Mr. Watts's labors were almost entirely of a literary character, and in this way he rendered English-speaking chemists the highest services. It appears that his family is left poorly provided for, and an attempt is to be made to secure, through subscriptions from chemists, a sufficient sum to keep them from want. A committee from English chemists have issued a circular from which the following quotation is taken:

"It having become known to some of the friends of the late Mr. Henry Watts, whose death occurred very suddenly on the 30th of last June, that his widow and family are in very straitened circumstances, an informal meeting was held at the Royal Institution on Tuesday, the 11th of this month. Those present resolved to form themselves into a Committee, with power to add to their number, in order to collect a fund for the benefit of Mrs. Watts and those of her children who are not of an age to provide for their own support. Dr. Atkinson consented to act as Secretary, and Dr. Perkin, President of the Chemical Society, as Treasurer.

"Mr. Watts's public labours for the advancement of Chemical Science may be said to have begun with the translation of Gmelin's 'Handbook of Chemistry,' the admirable English edition of which was prepared and edited for the Cavendish Society by him. This work occupies eighteen large octavo volumes, of which the first appeared in 1849, and the last in 1871. A work scarcely, if at all, inferior to this in magnitude, and one which has perhaps been of

even greater service to English chemists, both scientific and industrial, is Watts's great 'Dictionary of Chemistry,' which appeared from 1863 to 1881, in eight volumes, containing altogether nearly 9700 pages. Mr. Watts also edited and largely added to the second volume of the late Professor Graham's 'Elements of Chemistry,' published in 1858; he prepared several editions of Fowne's well-known 'Manual of Chemistry,' which he almost entirely rewrote and made into virtually a new work; and in conjunction with Mr. Ronalds and Dr. Richardson, he prepared for Messrs. Baillière, an elaborate treatise on Chemical Technology. Up to the time of his death, and for about thirty years previously, Mr. Watts was Editor of the Journal of the Chemical Society, and in this capacity, as well as in that of Librarian to the Chemical Society, he became personally known to and gained the friendship of very many among the Fellows of the Society."

Dr. Elwyn Waller, School of Mines, New York, will receive and forward subscriptions of American chemists.

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Cleve, Lecoq de Boisbaudran, et Sabatier. Métaux terreux. Glucinium, zirconium, thorium, cérium, lanthane, didyme, samarium, etc.

Guntz, A. Récherches thermiques sur les combinaisons du fluor.

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NIVOIT et MARGOTTET. Metaux alcalino-terreux. Baryum, strontium, calcium, magnesium, et aluminium.

POST, J. Traité complet d'analyse chimique appliquée aux essais industriels. Tradult de l'allemand par L. Gautier et P. Kienlen.

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IV.—GERMAN.

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BORGMANN, E. Anleitung zur chemischen Analyse des Weines. Weisbaden.

GODEFFROY. Tabellen und Formulare für qualitative und quantitative Analysen, Titrirmethoden, Harnanalysen, etc. Wien: Wallishausser.

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HOPPE-SEYLER, F. Ueber die Entwickelung der physiologischen Chemie, und ihre Bedeutung für die Medicin. Strassburg.

HUSEMANN, A., HILGER, A., und HUSEMANN, TH. Die Pflanzenstoffe in chemischer, physiologischer, pharmakologischer und toxikologischer Hinsicht. Für Aerzte, Apotheker, Chemiker und Pharmakologen bearbeitet. 2. völlig umgearbeitete Auflage. 2. Band. Berlin.

KREUSLER, M. Atomgewichtstafeln. Bonn: Weber.

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SCHELLHAMMER, H. Constructionen von Gasanalysenapparaten für die praktische Verwendung in Hüttenwerken und Fabriken. Leipzig.

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F. W. C.